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EFFECTS OF ANTI-ICING ADDITIVES ON JET FUEL PROPERTIES
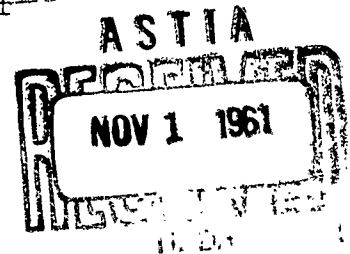
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PROPULSION LABORATORY
AERONAUTICAL SYSTEMS DIVISION
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UNITED STATES AIR FORCE
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MIDWEST RESEARCH INSTITUTE

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FOREWORD

This report was prepared by Midwest Research Institute under USAF Contract No. AF 33(616)-7598. The contract was initiated under Project No. 3048, Task No. 30178, "Effects of Anti-Icing Additives on Jet Fuel Properties." The work is administered under the direction of the Propulsion Laboratory, Wright Air Development Division, with Lt. John A. Hager acting as project initiator.

The period of research covered is from 1 September 1960 to 31 April 1961.

The work was carried out under the supervision of Mr. Daniel A. Netzel, Project Leader, and Mr. M. N. Schuler, Head, Industrial Chemistry Section. This report was prepared by Mr. Daniel Netzel.

Experimental work on the project was performed by Messrs. Thomas J. Byerley, and Harry Pollock. Supporting personnel to the project were Messrs. Lorren D. Kurtz, Gerald F. Bechtle, and Reid S. Flippin.

ABSTRACT

The storage stability of jet fuels containing anti-icing additive
P55MB has been investigated. Various storage stability tests were performed
at intervals during a storage period of five months. These tests include (1)
thermal stability, (2) gum content, (3) API gravity, (4) aniline point, and
(5) sulfide content. The effect of the additive on the extent of removal of
corrosion products by flaking was investigated. Also investigated was the
effect of the additive in promoting or limiting the growth of microorganisms
found in the natural water bottoms of fuel storage tanks.

The physical stability of solutions of additive P55MB in jet fuel
was studied. This investigation included: (1) the determination of the
partition coefficient between water and jet fuels for P55MB as a function of
temperature, (2) the maximum concentration of additive which can build up in
the water phase, (3) the solubility of each component of P55MB in jet fuels,
and (4) the "coupling effect" between the components of P55MB.

The water-retention characteristics of P55MB in jet fuel were also
studied.

The effects of anti-icing additives P55MB and Additive "A" on the
hardness of the topcoating of the fuel tanks were studied in detail. These
studies included (1) the effects of the additives in jet fuel and (2) the
effects of the additives in water. Both time and concentration effects were
determined.

A graphical relationship is given between the laboratory method and
the field method (Sward Rocker Hardness Test and Pencil Hardness Test, respec-
tively) of determining the hardness of the fuel-tank topcoating.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

MARC P. DUNNAM
Chief, Fuel and Oil Branch
Advanced Propulsion
and Subsystems Division
Propulsion Laboratory

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SUMMARY

An effective anti-icing additive, P55MB, which has been proposed for use in jet fuels, has been investigated to determine whether it adversely affects the performance of JP-4 and JP-5 jet fuels.

Fuel-storage stability studies were conducted. These tests determined the effect of P55MB on thermal stability, gum content, vapor pressure, sulfide content, aniline point, and API gravity. Analysis for the additive in fuel during the five-month storage period indicated a loss of additive of about 5 per cent for JP-4, and 11 per cent for JP-5 jet fuels. All other measured properties conformed to military specifications.

P55MB even in low concentrations can be expected to promote the growth of microorganisms found in the water bottoms of fuel storage tanks. The compounded additive and each of its components accelerated the growth, in sterile Bushnell-Haas media, of almost all of the 17 organisms found in fuel-tank water bottoms. Component G, which concentrates in the water phase, is especially active in promoting rapid growth of all organisms.

The partition coefficient of Component M between fuel and water was almost identical to that of P55MB itself. The partition coefficients increase as the temperature goes down and depend upon the concentration of Component M in the water phase. The maximum build-up of additive in the water phase at 30°F is less than the concentration of additive which will cause serious degradation of the fuel-tank topcoating.

The solubility of each component of P55MB was determined in JP-4 jet fuel. The solubility of Component M in jet fuel is decreased in the presence of Component G. Conversely, the solubility of Component G is increased in the presence of Component M.

Direct evidence for the "coupling effect" has been found. However, the absolute degree of coupling has not been determined.

Water-retention characteristics of P55MB were investigated. The rate of settling of micro-droplets of water is not affected by the presence of the additive.

A detailed study of the effects of the additive P55MB on the hardness of the fuel-tank topcoating was conducted.

Concentrations of P55MB below 0.5 per cent in fuel do not attack the fuel-tank topcoating. Varying the ratio of Component M to Component G of P55MB over a wide range showed little change in the action of the fuel phase on the topcoating resin. On the other hand, in the water phase, high concentrations of Component G greatly increase the resistance of the top-coating to attack by water.

Therefore, the proportion of Component G in P55MB should be set high enough to insure that a protective concentration of G is established in the water phase under normal conditions of use. The preferred level of G has not yet been determined, but will be limited by the low solubility of Component G in jet fuel.

Compatibility studies were conducted on an additional additive candidate (Additive "A") which exhibited anti-icing effectiveness. This compound showed topcoating attack in both the fuel and water phases. Unlike P55MB, no critical maximum concentration of the additive was found that was safe to use. The attack on the resin was directly proportional to the Additive "A" concentration in jet fuel.

I. INTRODUCTION AND OBJECTIVES

JP-4 fuel, which has been saturated with water at ambient ground temperature, loses its entrained water in the form of small ice crystals during high-altitude flight of the jet aircraft. Ice crystals have caused numerous operational difficulties and have also been implicated in aircraft failures.

A chemical approach - the addition of a compound to jet fuel to prevent or suppress the formation of ice - has been relatively successful.

Numerous anti-icing additives which are effective in preventing the formation of ice have been found. However, because of the chemical nature of these compounds, another serious problem becomes important: that is, the effects of these anti-icing additives upon the fuel-tank topcoating. The polar nature of the additives tends to solubilize or to degrade the Buna-N phenolic resin.

An additive has been developed which is an effective anti-icing agent, yet is compatible with the fuel-tank topcoating. This additive (Phillips Fuel additive 55MB) contains an inhibitor which prevents serious attack of the polar component on the Buna-N phenolic resin.

Before government approval can be given for the use of this additive in jet fuel, numerous tests must be made. These tests include the following:

1. Determination of the effectiveness of the additive in suppressing ice formation at various concentrations (of the additive) in jet fuel.

2. A study of the compatibility of the additive with fuel-tank topcoating.

3. Studies on the depletion of the additive into a discrete water phase.

4. A determination of the maximum concentration of additive which can build up in the water phase as a function of temperature.

5. Studies of the effects of the additive on the storage stability of the fuel.

6. A study of the effects of the additive on the physical properties and burning characteristics of the jet fuel.

The above list, although not complete, enumerates the important tests.

Midwest Research Institute has undertaken a contract to determine as many of the following characteristics of the fuel-additive system as possible during the allotted time. These studies include:

1. Determination of the effects of the additive upon the storage stability of the fuel. These tests included: thermal stability, gum content, vapor pressure, sulfide content, aniline point, and API gravity.

2. Determination of the effects of the additive on the removal of corrosion products from storage tanks, pipelines, etc.

3. Determination of the role of P55MB in the growth of microorganisms at both the fuel-water interface and the water bottoms of the fuel storage tanks.

4. Determination of the partition coefficient of P55MB between the water phase and fuel phase as a function of temperature.

5. Determination of the compatibility of the additive with the fuel-tank topcoating as a function of time, concentration, and per cent inhibitor (Component G) in P55MB.

These five studies were carried on for JP-4 and JP-5 fuels.

II. STORAGE STABILITY OF FUEL CONTAINING ANTI-ICING ADDITIVE P55MB

A. Discussion of Results and Conclusions

1. Additive Effects on Properties Subject to Change During Storage

The effects of P55MB anti-icing additive during storage can change the performance of JP-4 and JP-5 jet fuels by changing the properties: thermal stability, gum content, vapor pressure, sulfide content, and thermal value (API gravity times aniline point).

The various properties of the jet fuels measured at intervals throughout the test period of five months are given in Tables VI and VII (see Appendix I, p. 52).

The amount of additive in each storage drum was measured at intervals throughout the storage period. The minimum and maximum temperatures were also recorded for each day on which samples were removed from the storage drums.

An initial drop in additive concentration took place during the first two months of storage. Afterward the concentration remained nearly constant. Table I gives the per cent loss of additive for JP-4 and JP-5 jet fuel containing 0.1 and 0.2 per cent additive. Also contained in Table I is the average per cent loss of additive in closed and opened vented drums.

TABLE I

PER CENT LOSS OF ADDITIVE DURING STORAGE

Jet Fuel	Closed Vents		Open Vents	
	0.1%	0.2%	0.1%	0.2%
JP-4	4	7	8	5
Avg.	5.5		6.5	
JP-5	14	8	14	15
Avg.	11.0		14.5	

The amount of additive loss during storage from JP-4 jet fuel was 5.5 per cent, one-half the per cent loss of additive from JP-5 jet fuel (11.0 per cent). The per cent loss of additive in JP-4 and JP-5 jet fuels increased when the drums were vented to the atmosphere.

Thermal stability of the jet fuels also decreased sharply after the first two months of storage, and then remained nearly constant throughout the remaining test period. However, since the thermal stability of the jet fuels

without the additive also decreased in the same manner, the change in the thermal stability due to the additive was negligible. Additive concentrations of 0.1 and 0.2 per cent in the jet fuels had no significant effects on this thermal stability.

Both the existing and potential gum contents of JP-4 and JP-5 jet fuels were measured.

No measurable changes in the existing gum content with time or concentration for JP-4 and JP-5 jet fuels could be determined. However, the total potential residue for JP-5 jet fuel decreased with time, and increased with concentration of the additive in the fuel. These differences were most noticeable for those drums of fuel which had been vented to the atmosphere.

The total potential residue for JP-4 jet fuel decreased with concentration and increased with time. Again, the effects were most noticeable for those drums of fuel which had been vented to the atmosphere.

The Reid vapor pressure, thermal value (API gravity times aniline point), and copper corrosion test for JP-4 and JP-5 jet fuels were measured, but the data were insensitive to time conditions and concentration of the additive in the jet fuels.

All data obtained on the properties of the jet fuels during the storage period were within the specifications as outlined in the Military Specification Mil-J-5624E.

2. Additive Effects on Fuel Contamination

The Air Force has noted that jet fuel tends to loosen particles of lint or rust from the surface of tanks, pipelines, etc., and thereby becomes contaminated. The effect of the additive on promoting or limiting this flaking action was investigated. However, time did not permit a detailed study, and results obtained were not conclusive.

Two and two-tenths milligrams of rust deposit were collected from jet fuel containing 0.2 per cent additive as compared to 2.0 mg. of deposit from jet fuel without additive. It is doubtful that this small difference is significant.

3. Additive Effects on Bacterial Growth

Bacterial growth in the water bottoms of fuel storage tanks can, if pumped aboard the aircraft, present operational problems. The use of additives in the jet fuel may promote or accelerate the growth of the numerous types of microorganisms found at the fuel-water interface and in the aqueous phase. On the other hand, an additive could possibly decrease the growth of the microorganisms.

Bacteriological studies have been conducted to determine the effects of the anti-icing additive P55MB in Bushnell-Haas salts solution on 18 different microorganisms. The organisms consisted of three fungi and 15 gram negative and gram positive organisms. Two per cent and 10 per cent concentrations of additive were used. Eight days after inoculation, 16 of the 17 cultures showed growth in the 2 per cent concentration. One inoculum consisted of a mixture of two bacterial cultures. Twelve out of 17 cultures showed growth in the 10 per cent concentration after eight days.

Increasing the concentration of the additive in the B-H salts solutions decreased the microorganism growth in all cultures studied. These results were obtained by visual observations and are listed in Table II (Section II, B, 3, p. 13).

To determine which component of P55MB was most susceptible to attack by the microorganisms, 2 per cent solutions of Component M and Component G, each in B-H salts solutions, were inoculated with the 17 cultures.

The 2 per cent solution of Component M showed less growth over the same period of time than the 2 per cent solution of P55MB. Nevertheless, growth did occur in 13 out of the 17 cultures.

The 2 per cent solution of Component G showed equal or greater growth in 16 out of 17 cultures over the same period of time than the 2 per cent solution of P55MB. Two cultures, 525X and 579 (unidentified) liberated gas when Component G was metabolized in B-H salts solutions.

The results indicate that the additive P55MB will not limit the growth of most of the microorganisms found in the water bottoms of jet fuel storage tanks.

Since the additive does support growth of the microorganisms, it may also promote the growth of these microorganisms in jet fuel. More exhaustive tests were conducted.

Figures 2, 3, 4, 5, 6, and 7 (pp. 15, 16, and 17) show the growth of six microorganisms in the B-H salts solution with time.

Microorganisms 6011 and Bacillus pumilus showed definite increase in growth because of the additive, while microorganisms DD2, CSE and PJ-2 showed no change. Only microorganism 519 showed a definite decrease in growth due to the presence of P55MB.

From the photographs, Figs. 8 and 9, p. 18 and p. 19, it appears that the mold Cladosporium resinae definitely increased in growth in the presence of P55MB.

It is concluded from these data that the additive P55MB will promote or limit the growth of microorganisms in the natural water bottom of fuel storage tanks, depending upon the type of organism.

B. Experimental

This section describes the procedure for the preparation of the fuels prior to storage.

Six 55-gal. drums each of JP-4 and JP-5 were used in the tests.

To four drums (two of JP-4, two of JP-5 fuel) no additive was added; to the second set of four drums (two of each fuel), 208 ml. of P55MB were added; and to the last set of four drums (two of JP-4, two of JP-5 fuel), 416 ml. of P55MB were added. The additive was mixed into the fuels with a compressed-air-driven stirrer for 5 min. After 4 hr., samples were removed from each of the drums to be used for the various tests mentioned above. The additive concentration was determined volumetrically from the procedure developed by Phillips Petroleum Company.

After the initial sampling, the drums of JP-4 and JP-5 fuels were stored out of doors at Deramus Field Station south of Kansas City, Missouri. The ambient temperatures were those of winter and early spring at that location.

One drum each of 0.0, 0.1, and 0.2 per cent concentration of P55MB in both JP-4 and JP-5 were stored with open vents. The remaining drums were stored with closed vents.

Samples were drawn every two months after the date of the initial sampling. The preparation of the drums for storage was staggered over one month to keep analysis current with sampling.

The specific experimental procedures for the various tests are given below:

1. Additive Effects of Properties Subject to Change During Storage

a. Thermal stability: The experimental determination of the thermal stability of JP-4 and JP-5 jet fuels was subcontracted to Phoenix Chemical Laboratory, Chicago, Illinois. The thermal stability was determined by the use of an ASTM-CFR Fuel Coker according to the ASTM Text Method D1660-59T.

b. Gum content: The gum content of JP-4 and JP-5 fuels containing P55MB anti-icing additive was also subcontracted to Phoenix Chemical Laboratory. They measured both the potential and existing gum contents according to ASTM Test Methods D381-58T and D873-57T.

c. Vapor pressure, sulfide content, and thermal value: The Reid vapor pressure determination and the sulfide content determination of the fuels were performed at MRI. The procedures used were those of ASTM Test Methods D323-58 and D130-56, respectively.

The thermal value is the aniline-gravity product. Both the aniline point and the API gravity determinations were performed according to ASTM Test Methods D611-55T and D287-55, respectively.

d. Specific conductivities: The determination of the specific conductivity of the fuels-additive mixture was attempted. It was hoped that these values could be related to the increase or decrease in the static potentiality of fuels. However, no reliable and reproducible data could be obtained because of the lack of proper instrumentation.

The results of the above experiments of the physical properties of jet fuel during storage are given in Tables VI and VII, pp. 53 and 57.

2. Additive Effects on Fuel Contamination

The effect of the additive on promoting or limiting the action of corrosion removal was investigated in the following manner: metal strips

(1 x 4 in.) from line pipe utilized in transferring jet fuel conforming to API specification 5LX was initially cleaned and then corroded by subjecting the strips to a water spray at 75°F for 48 hr. After the corrosion had taken place, the strips were dried. Strips of metal were suspended in pre-filtered JP-4 fuel and 0.2 per cent additive-fuel mixture. The metal strips were then rotated at 34 rpm for 8 hr. The corroded metal strips were removed and the fuel filtered through filter paper. The filter paper was washed with acetone and dried. The increase in weight of the filter paper was a measure of the amount of corrosion product removed in the fuel and in the additive-fuel mixture.

Figure 1 is a photograph of the instrument used for the corrosion experiments.

3. Additive Effects on Bacterial Growth

Experiments were performed to determine the effects of P55MB jet-fuel anti-icing additive and its components on the growth of 16 cultures of microorganisms isolated from natural water bottoms of fuel storage tanks. Two cultures (Bacillus pumilus and Bacillus cereus)* have not been fully tested for growth at the interface of water and jet fuel.

Thirteen test samples were inoculated with bacterial cultures, while one inoculum consisted of a mixture of two bacterial cultures. Three test samples were inoculated with fungi.

The names or culture designations of the microorganisms used in the experiments are listed in Table II. A few cultures have been partially identified. The unknown cultures are now being identified.

The experimental procedure for determining the effects of these microorganisms on P55MB and its components is as follows.

A Bushnell-Haas salts solution having the following composition was prepared.

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* Obtained from the University of Kansas City culture collection.
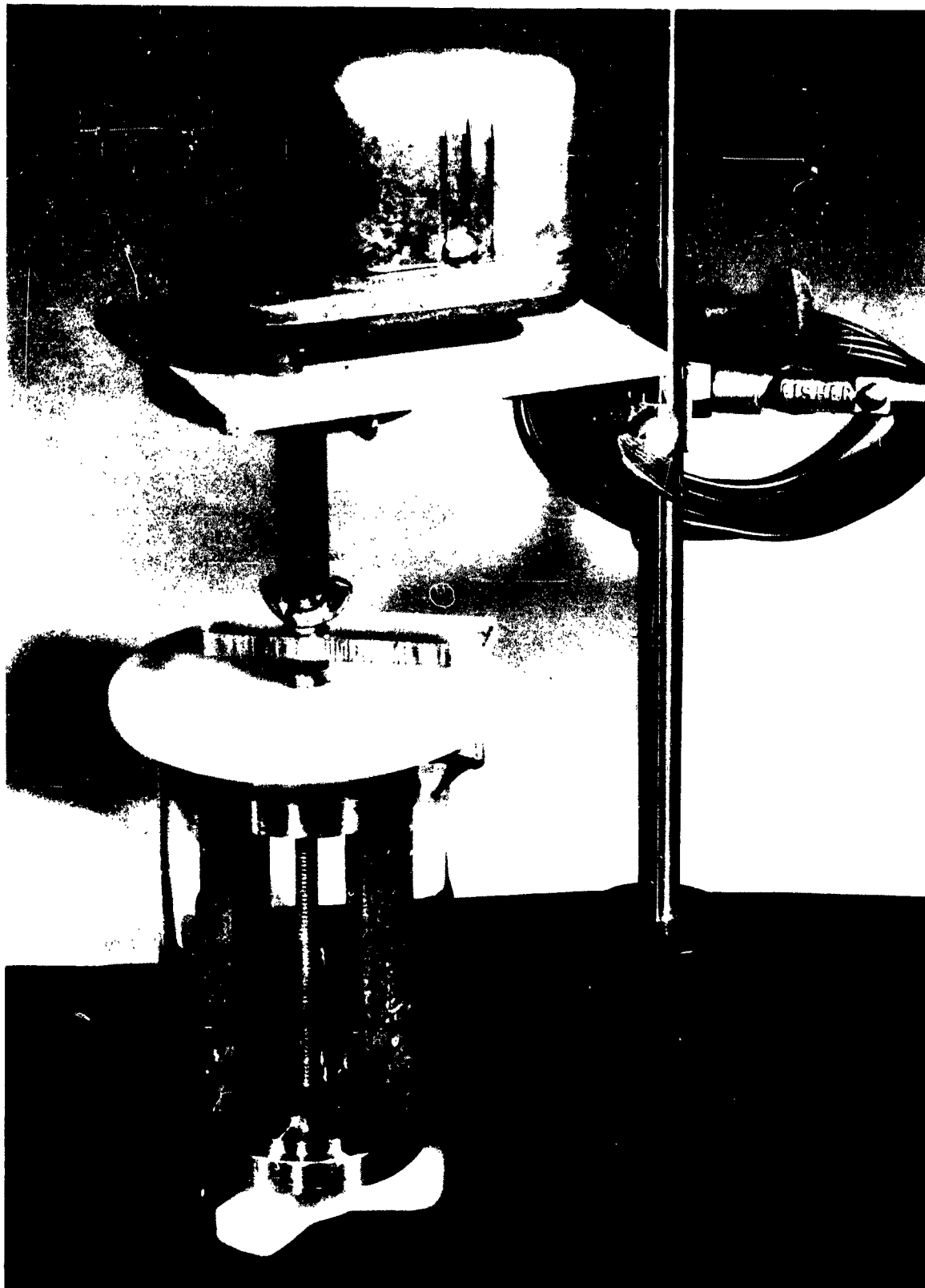
Fig. 1 - Corrosion Test Apparatus

Distilled Water	1 liter
Magnesium Sulfate ($MgSO_4$)	0.20 g.
Calcium Chloride ($CaCl_2$)	0.02 g.
Potassium Dihydrogen	
. Phosphate (KH_2PO_4)	1.00 g.
Dipotassium Hydrogen	
Phosphate (K_2HPO_4)	1.00 g.
Ammonium Nitrate (NH_4NO_3)	1.00 g.
Ferric Chloride ($FeCl_3$)	0.05 g.

Five milliliters of B-H salts solution was placed into test tubes. A small piece of iron nail was added to simulate the steel of the storage tank on the basis of studies at MRI which have shown that iron must be present to promote _in vitro_ growth of some organisms isolated from natural water bottoms of fuel tanks. Unsterilized P55MB was added to the test tubes containing the B-H salts solutions until concentrations of 2 per cent and 10 per cent were obtained. The tubes were then inoculated with the 18 cultures of microorganisms. After eight days the growth of the microorganisms was visually compared to a control test tube of the medium alone.

Two per cent solutions of each of the components (M and G) of P55MB were prepared in the same manner as described above. Again after eight days, the growth of the microorganism was visually compared to a control sample. The results are listed in Table II.

The conclusions drawn from the above data on the effects of P55MB on the growth of microorganisms in the natural water bottoms of fuel storage tanks indicated that the organisms will grow on P55MB. However, the data were incomplete, and did not show whether the additive would promote the growth of these microorganisms.

Tests were designed to determine this effect of P55MB on six bacterial cultures and one mold culture. These cultures are identified as follows:

1. 6011;
2. DDS-2;
3. 519 (Pseudomonas Species);
4. CSE;
5. PJ-2;
6. Bacillus pumilus; and
7. Cladosporium resinae (mold).

TABLE II

GROWTH OF MICROORGANISMS IN B-H SALTS SOLUTIONS OF P55MB
ANTI-ICING ADDITIVE
(Elapsed Time After Inoculation - 8 Days)

Name of Microorganism		Concentration of P55MB in B-H Salts Solution		Concentration of Component M in B-H Salts Solution	Concentration of Component G in B-H Salts Solution
		(2%)	(10%)	(2%)	(2%)
Control Sample		-	-	-	-
Bacteria					
*Bacillus pumilus	G⁺	++	+	+	++
*Bacillus cereus	G⁺	++	+	+	+
PJ-2	G⁻	++	+	+	++
DDS-2	G⁻	+++	-	++	++
6011	G⁻	+++	-	+	++
GL-20	G⁻	+	+	+	+
CSE	G⁻	+++	-	-	+++
Pseudomonas species	G⁻	+++	+	-	-
KS-5r	G⁻	+	+	+	+
KS-5xs	G⁻	+	+	+	+
525x	G⁻	+++	-	++	++++(gas)
579	G⁻	+++	+	++	++++(gas)
CSIw+CSIy	G⁻	+++	+	++	++
Mycobacterium species	G⁺	-	-	+	+
Fungi					
Cladosporium resinae strain 1		+	+	-	++
Cladosporium resinae strain 2		+++	+++	-	++
Candida lipolytica		+++	+	+	++

Legend:

++++ = Heavy growth

+++ = Good growth

++ = Fair growth

+ = Poor growth

- = No growth

* Cultures obtained from the University of Kansas City.

JP-4 jet fuel samples containing 0.0, 0.1, and 0.2 per cent P55MB were placed above B-H salts solutions. The water phase was then inoculated with one of the cultures. The procedure was the same for the remaining six cultures. After a given time interval, counts of the organisms were made to determine if P55MB promoted the growth of these microorganisms.

Figures 2, 3, 4, 5, 6, and 7 are plots of the total count of the microoroganism versus time for the six cultures studied. Figures 8 and 9 are photographs of the fuel-additive mixtures just inoculated with the mold Cladosporium resinae and after one month of growth, respectively.

III. SOLUTION STABILITY OF ADDITIVE-FUEL BLENDS

A. Discussion of Results and Conclusions

1. The Partition Coefficient Between Water and Jet Fuels for Component M of P55MB Anti-Icing Additive

Because of the compatibility problem, it was essential to determine the maximum additive concentration which can build up in the water remaining in the aircraft fuel tanks. The distribution of Component M of P55MB between water and the jet fuels has been studied as a function of temperature.

The results clearly indicate that as the temperature decreases, the partition coefficient increases (Fig. 15, Section III, B, 1, p.27). The results also indicate that the partition coefficient is a function of the concentration of Component M in the water phase, and that this functionality is not constant but increases with decreasing temperatures.

This deviation from ideal conditions is due to the association and dissociation of Component M in either or both of the phases. Since the deviation was found to be greater than 1.0, less association of Component M occurs in the water phase than in the fuel phase.

The increase of Component M in the water phase can be explained by the decrease in solubility of Component M in the fuel phase as the temperature decreases.
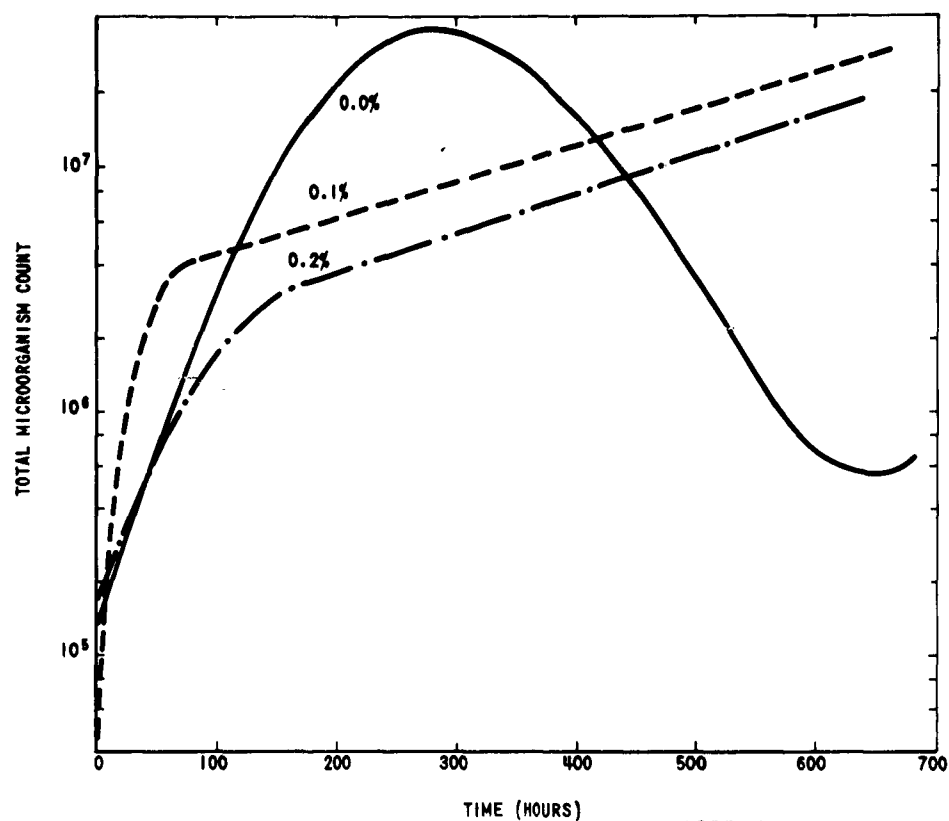
Fig. 2 - Growth of Microorganism No. 6011 in B-H
Salts Solution Phase
(% P55MB in JP-4 Jet Fuel Phase)
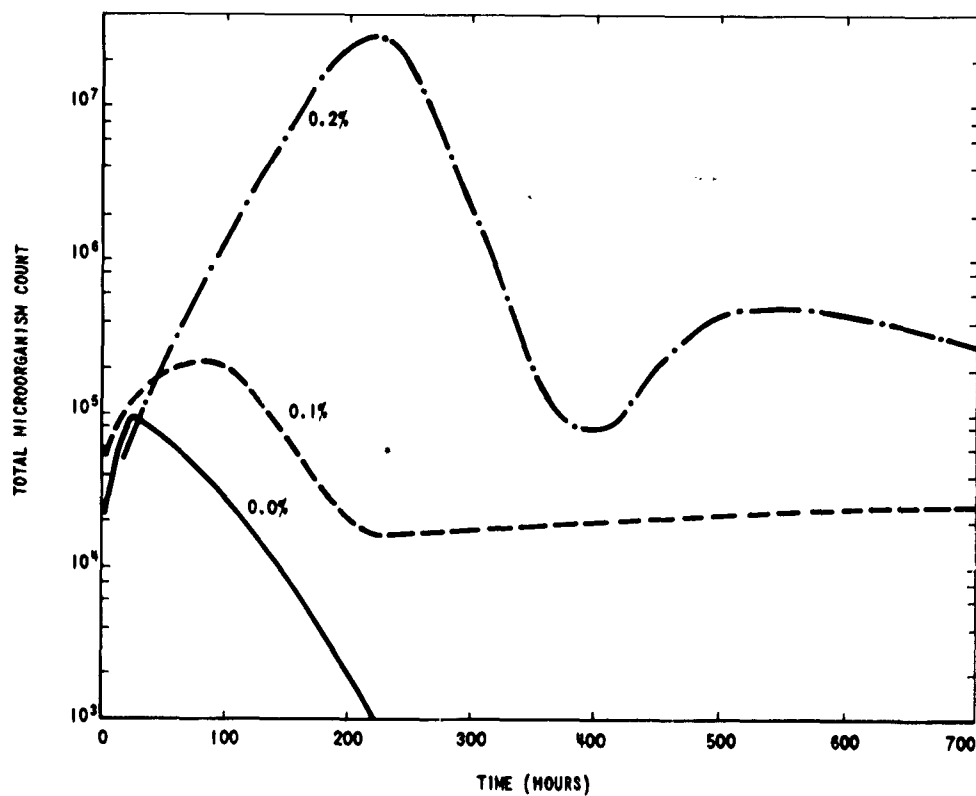
Fig. 3 - Growth of Microorganism Bacillus pumilus
in B-H Salts Solution Phase
(% P55MB in JP-4 Jet Fuel Phase)
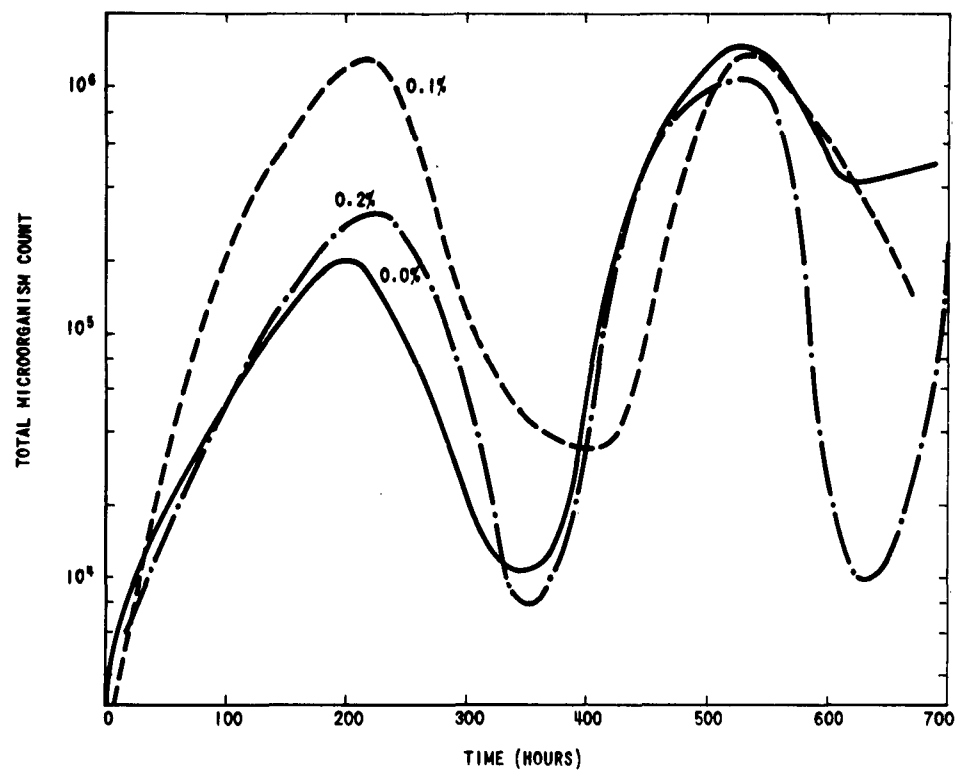
Fig. 4 - Growth of Microorganism No. DDS-2 in B-H
Salts Solution Phase
(% P55MB in JP-4 Jet Fuel Phase)
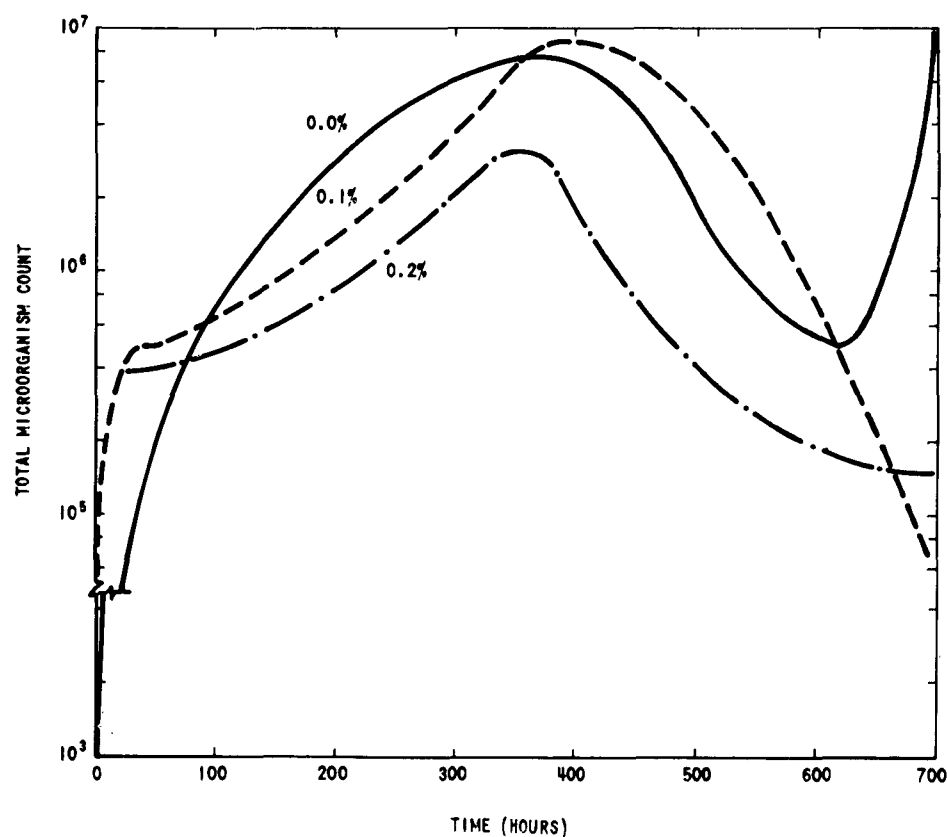
Fig. 5 - Growth of Microorganism No. CSE in B-H
Salts Solution Phase
(% P55MB in JP-4 Jet Fuel Phase)
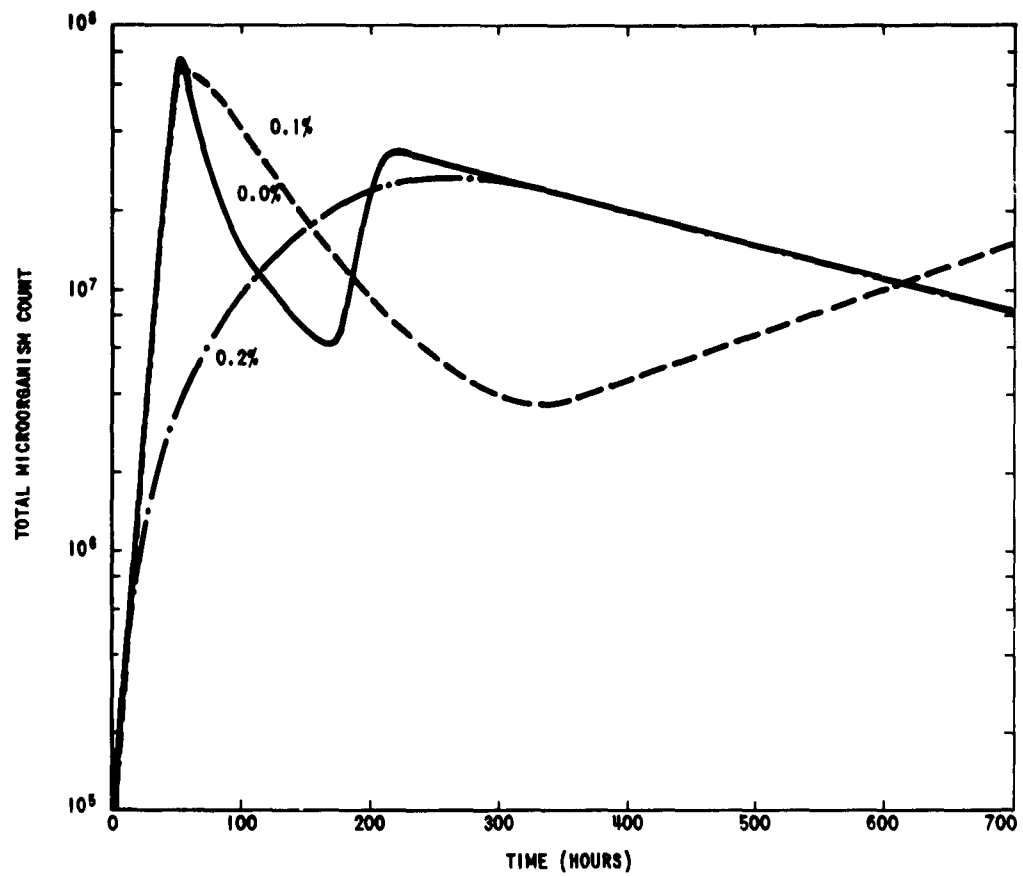
Fig. 6 - Growth of Microorganism No. PJ-2
in B-H Salts Solution Phase
(% P55MB in JP-4 Jet Fuel Phase)
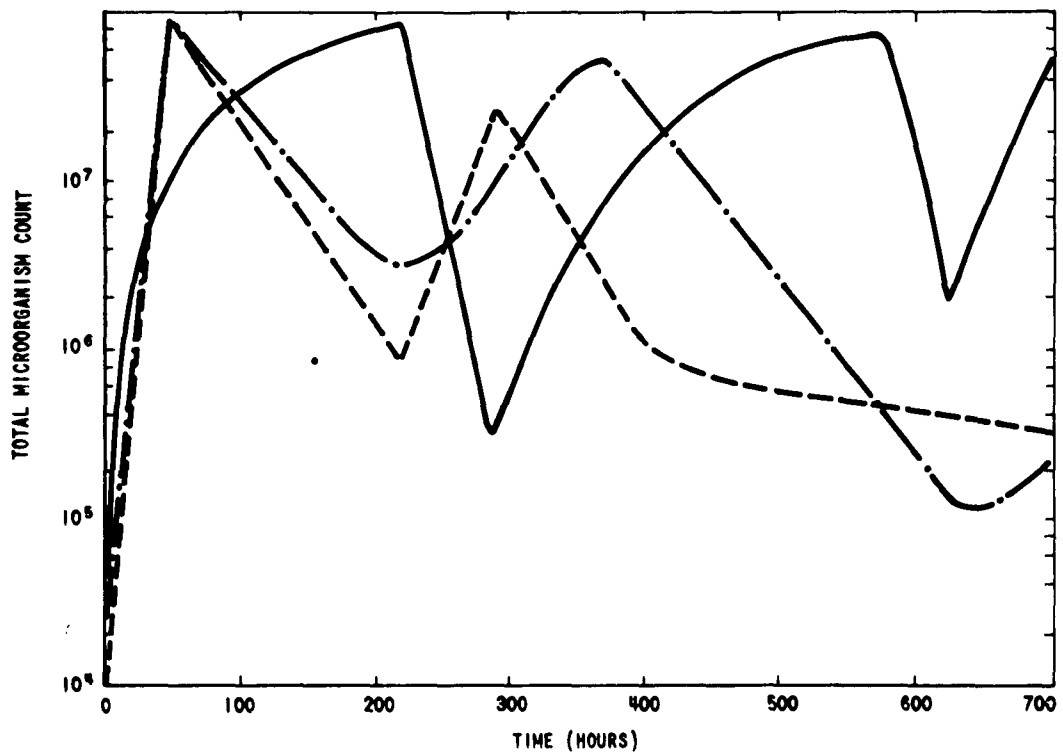
Fig. 7 - Growth of Microorganism No. 519
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(% P55MB in JP-4 Jet Fuel Phase)
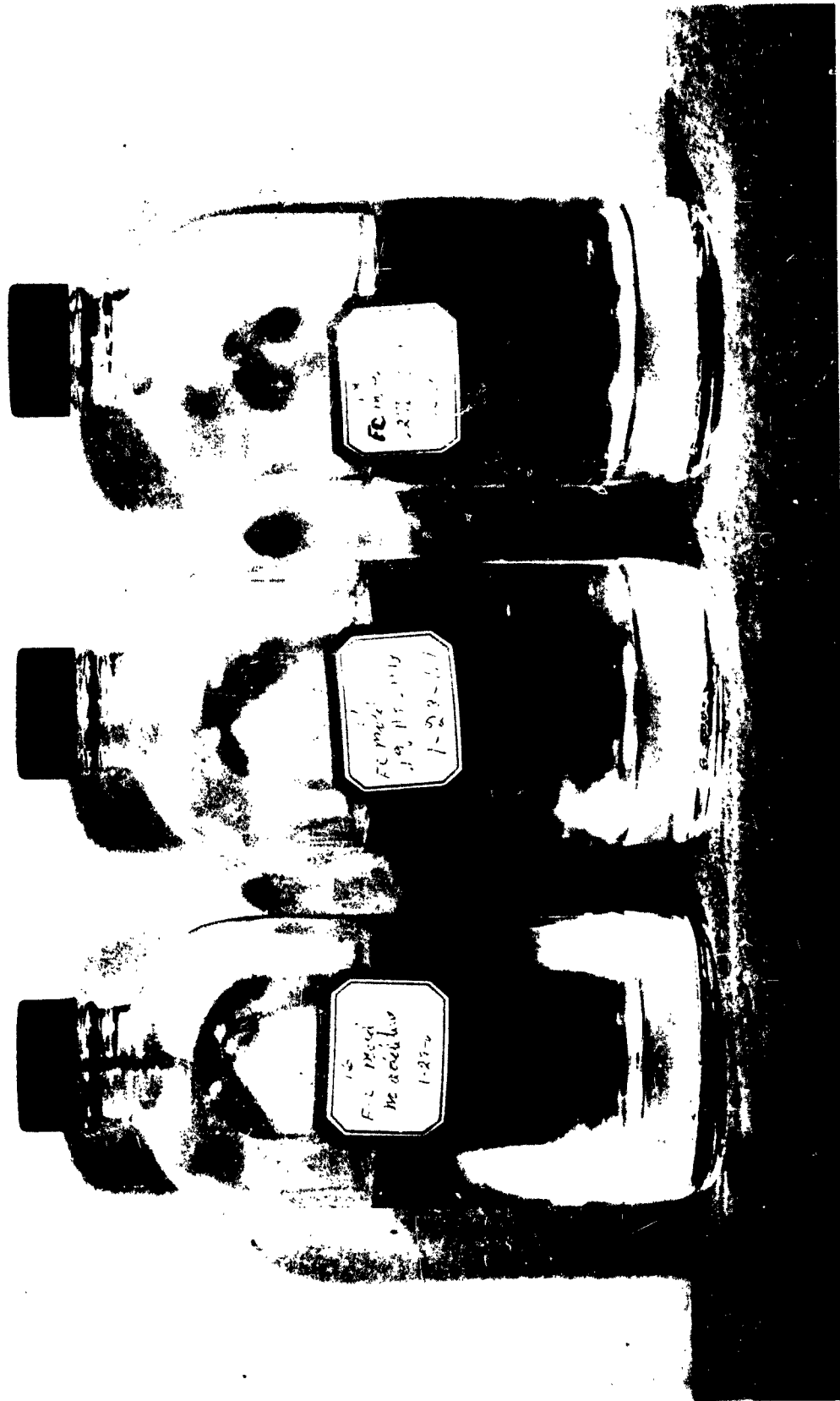
Fig. 8 - Initial Inoculation of B-H Salts Solution Phase with Mold
Cladosporium resinae. JP-4 Jet Fuel Phase
(A) 0.0% P55MB, (B) 0.1% P55MB, (C) 0.2% P55MB
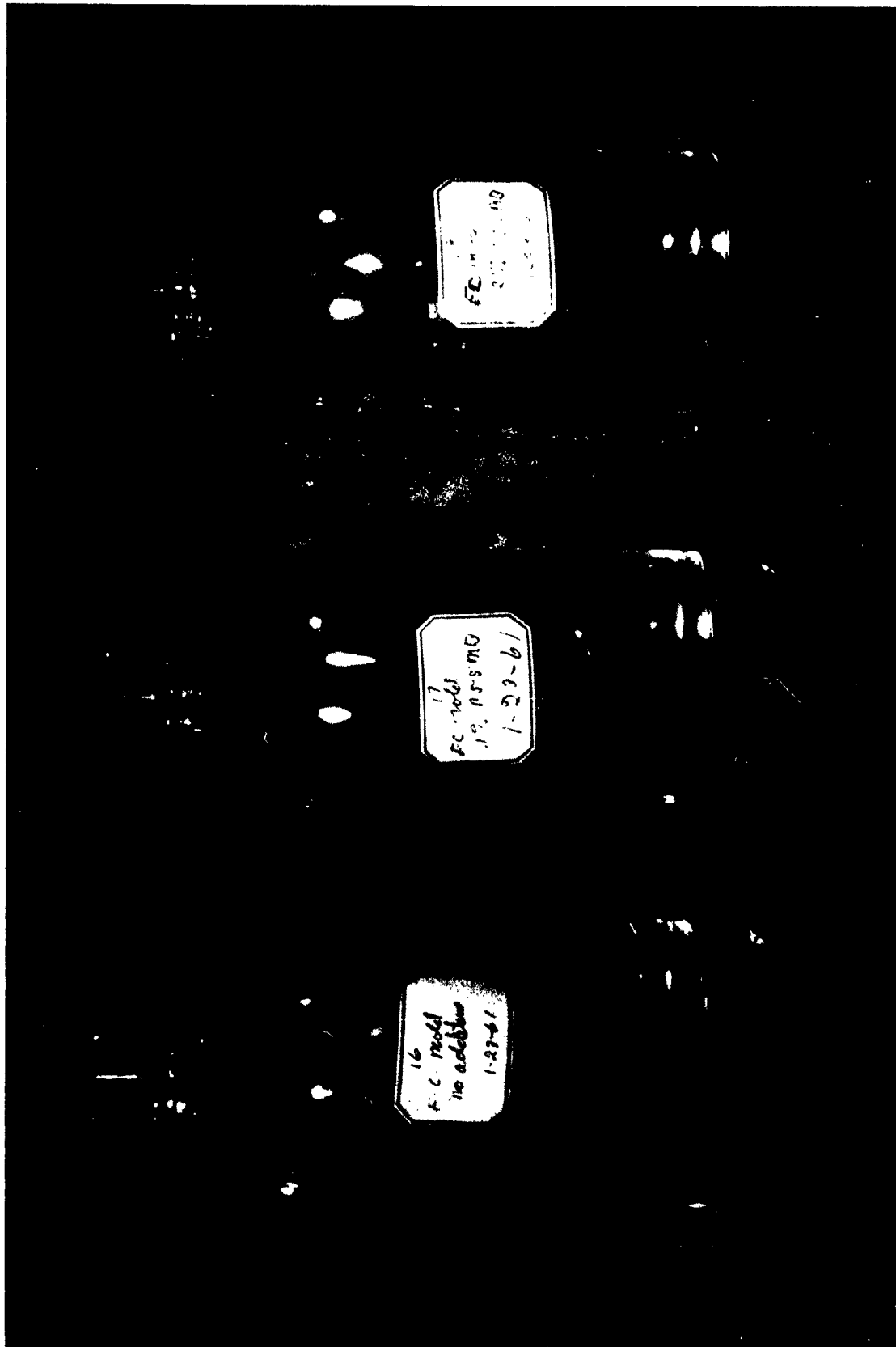
Fig. 9 - Growth of Mold Cladosporium resinae After One Month in B-H Salts Solution Phase. JP-4 Jet Fuel Phase, (A) 0.0% P55MB, (B) 0.1% P55MB, (C) 0.2% P55MB

The partition coefficients of Component M in JP-4 and JP-5 were found to be nearly identical. The behavior of the partition coefficient with increasing concentration of Component M in the water phase over a temperature range of 41 to 140°F is also nearly the same.

The partition coefficient of Component M between water and JP-4 was found to be 120. This value is 25 per cent lower than the value published in WADD Technical Report 60-226 under the same set of conditions. However, the maximum amount of Component M that will build up in the water phase is the same (32 per cent) if the effect of the concentration of Component M on the partition coefficient is taken into account.

The maximum concentration of Component M which can be built up in the water phase at 41°F was calculated to be 47 per cent if the ratio of water to fuel (containing 0.2 per cent additive) is maintained at 1:100. However, it is not improbable that the maximum concentration of Component M in the water phase can increase to a value of 50 per cent or more if the temperature is reduced to 30°F or lower.

The values of the maximum concentration of Component M in the water phase, when the fuel phase contains 0.1 per cent Component M, is not exactly one-half of the above figures. One must take into account the effect of the concentration of Component M in the water phases on the partition coefficient.

The equation relating the maximum concentration of the additive that can build up in the water phase with the temperature and concentration of additive in the fuel phase was derived. For simplicity, a graph was constructed relating the maximum concentration of the additive that can build up in the water phase to the temperature (see Fig. 16, p.28). The two curves represent 0.1 and 0.2 per cent additive concentrations in jet fuel. The volume ratio of jet fuel to water will determine the number of extractions necessary to reach maximum buildup of additive in the water phase.

2. Solubility of P55MB in JP-4 and JP-5 Jet Fuels

The solubility of P55MB in JP-4 and JP-5 has been determined. Figure 17, p. 30, shows the solubility of P55MB in JP-4 and JP-5 jet fuels as a function of temperature. For any given temperature, P55MB is more soluble in JP-4 jet fuel than in JP-5 jet fuel. However, in both fuels, the solubility of P55MB at -65°F is greater than 0.3 per cent.

The results indicate that no serious loss of concentration of additive in jet fuel will be encountered as the temperature is lowered if the total concentration of additive in fuel is less than 0.3 per cent.

3. "Coupling Effect" Between Component M and Component G

There is reason to believe that a finite amount of Component G remains in the fuel after the first extraction of additive with water. The amount of Component G remaining in the fuel can possibly be explained by the "coupling effect" of Component M and Component G.

The effect of one component on the solubility of the second component was studied in an effort to determine the degree of coupling. The solubility of Component M alone, and its solubility in the presence of Component G, were determined. A definite decrease in solubility of Component M in jet fuel was noted when Component G was present (see Fig. 18, p. 32).

The determination of the solubility of Component G was exceedingly difficult. However, some data have been obtained (see Fig. 19, p. 32). The solubility of Component G in jet fuel seems unreasonably high. These results may be due to dispersed micro-droplets of Component G in the jet fuel. If so, the data are still valuable in that they would represent the trend in the degree of solubility of Component G in jet fuel.

The solubility of Component G increased in the presence of Component M over the temperature range studied (see Fig. 19).

Though the data do not give the absolute degree of coupling, they indicate that the process of coupling definitely occurs and that the degree of coupling increases as the temperature increases.

4. Water-Retention Characteristics of P55MB in Jet Fuel

Micro-droplets of water form in water-saturated jet fuel when the temperature is lowered. In a large storage tank the rate of sedimentation is very slow.

An experiment was designed to determine if the sedimentation rate of water in jet fuel is increased or decreased in the presence of anti-icing additive P55MB.

Water-saturated jet fuel samples with and without the additve were cooled and the turbidities of the solutions recorded. Although the additive in fuel solubilized much of the water, the rate of sedimentation of the micro-droplets of water is the same for jet fuel with and without P55MB (see Fig. 20, p. 34).

The additive P55MB does not affect the water-retention character-istics of jet fuel.

B. Experimental

1. Partition Coefficient of P55MB Between Jet Fuel and Water

Partition coefficients have been determined at three temperatures (41°, 75°, and 140°F) for the solute, Component M of P55MB, between the JP-4 or JP-5 jet fuels and water. Component M was used initially in this work rather than P55MB itself to simplify the extraction procedure and the evaluation of the data. After the techniques had been mastered, experiments were performed with P55MB in place of Component M.

The partition coefficient values agree with the values obtained when Component M of P55MB is used. Therefore, the data obtained for Com-ponent M can be used for P55MB.

One method of determining the partition coefficient is as follows:

The volume of water used to extract the additive from the fuel in the first extraction is placed in a second separatory funnel. The extrac-tion of the additive from a second fuel-additive phase is performed. The water phase is then separated and placed into a third separatory funnel, and the procedure is repeated for some set number of extractions. After every extraction the concentration of additive in the water phase is meas-ured until the increase of the concentration of the additive in the water phase can no longer be detected. Errors due to repeated phase separation and volume transfer losses can be serious when this procedure is used. To eliminate errors during multiple extraction, single extractions of the ad-ditive from the fuel were performed with water solutions initially contain-ing 0, 5, 10, 20, 30, and 35 per cent of Component M.

The decrease in additive concentration in the fuel phase after each extraction was measured. This procedure is nearly the same as that

described in WADD Technical Report 60-226, p. 47, except that the amount of Component M remaining in the fuel phase was determined instead of the amount of increase of Component M in the water phase. This change in procedure was necessary since a more direct and accurate analysis could be made for the amount of Component M in the fuel phase.

Prior to the determination of the extent of extraction of Component M into the water phase, the fuel phase containing 0.2 per cent of Component M was shaken for 5 min. with the water phases containing the various percentages of Component M. After shaking, the system was allowed to stand 1 hr. before a sample of the fuel phase was removed for analysis.

A volume ratio of 100/1 of JP-4 and JP-5 fuel to water was maintained throughout the experiments.

The concentration of Component M remaining in the fuel phase was determined volumetrically by a procedure developed by Phillips Petroleum Company.

The partition coefficient was determined at 41°F by performing the extractions in a "cold room" after thermal equilibrium had been established. The necessary titrations, however, were performed at room temperature (75°F).

The partition coefficient at 140°F was determined by performing the extraction in an oven maintained at a constant 140°F. Since the doors of the oven had to be opened for sampling the fuel phase, the temperature of the fuel may have been slightly less than the oven temperature.

Figure 10 shows the distribution of Component M, expressed in grams per milliliters, in JP-4 jet fuel and water as a function of the temperature. Figure 11 gives the same information for JP-5 jet fuel. The resulting curves shown on the two graphs indicate that the partition coefficient is dependent upon the concentration of Component M in the water phase. A straight-line function would have indicated lack of a dependence upon concentration.

However, if the data are plotted on log-log paper as suggested by J. A. Campbell,[1] straight lines are obtained; these can be extrapolated to zero concentration to yield values which are related to the partition coefficient (Figs. 12 and 13). The reciprocal of the extrapolated values obtained equals the partition coefficient.

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[1] Campbell, J. A., Ind. and Eng. Chem., 36, 1158 (1944).
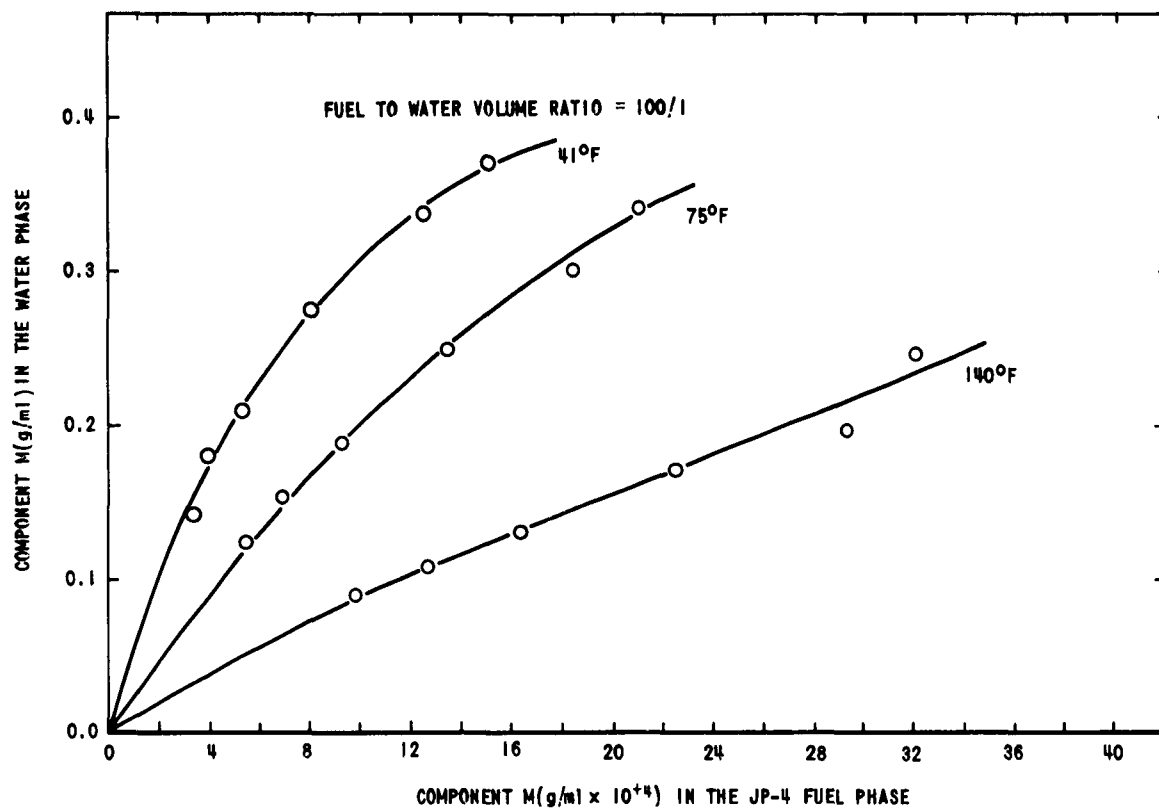
Fig. 10 - Partition Data as a Function of Temperature for
Component M of P55MB Anti-Icing Additive
Between Water and JP-4 Jet Fuel
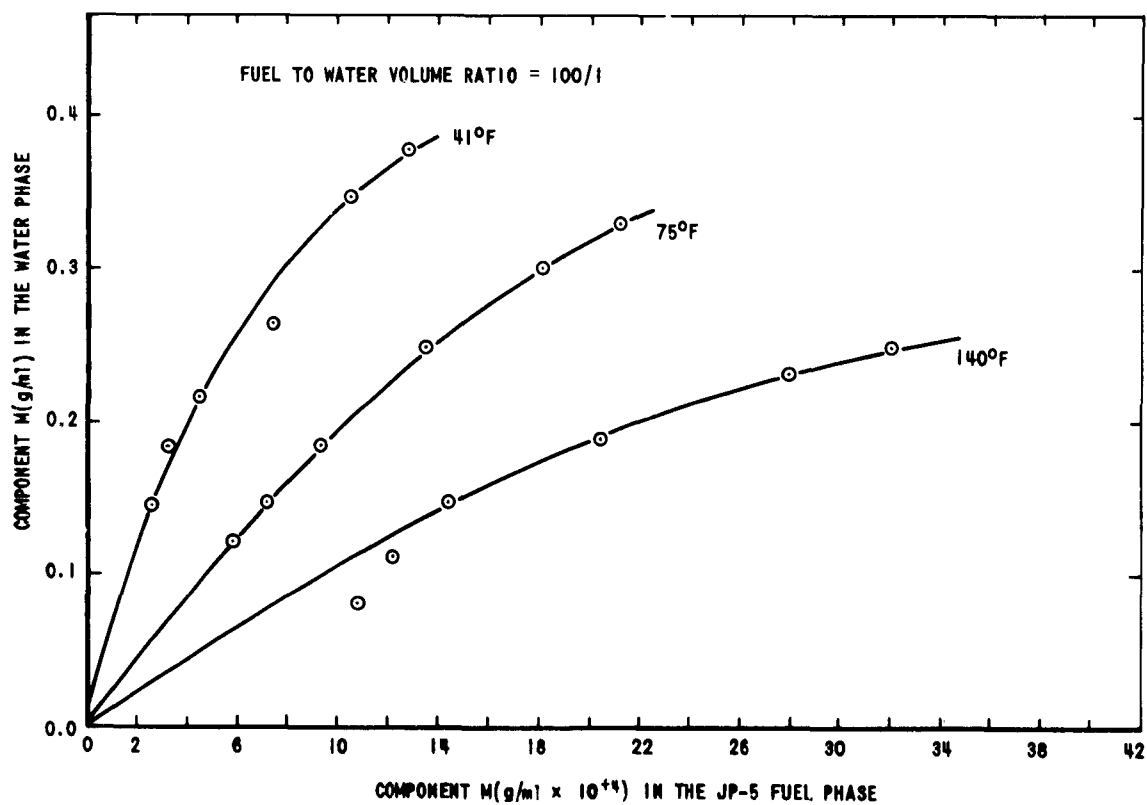
Fig. 11 - Partition Data as a Function of Temperature for
Component M of P55MB Anti-Icing Additive
Between Water and JP-5 Jet Fuel

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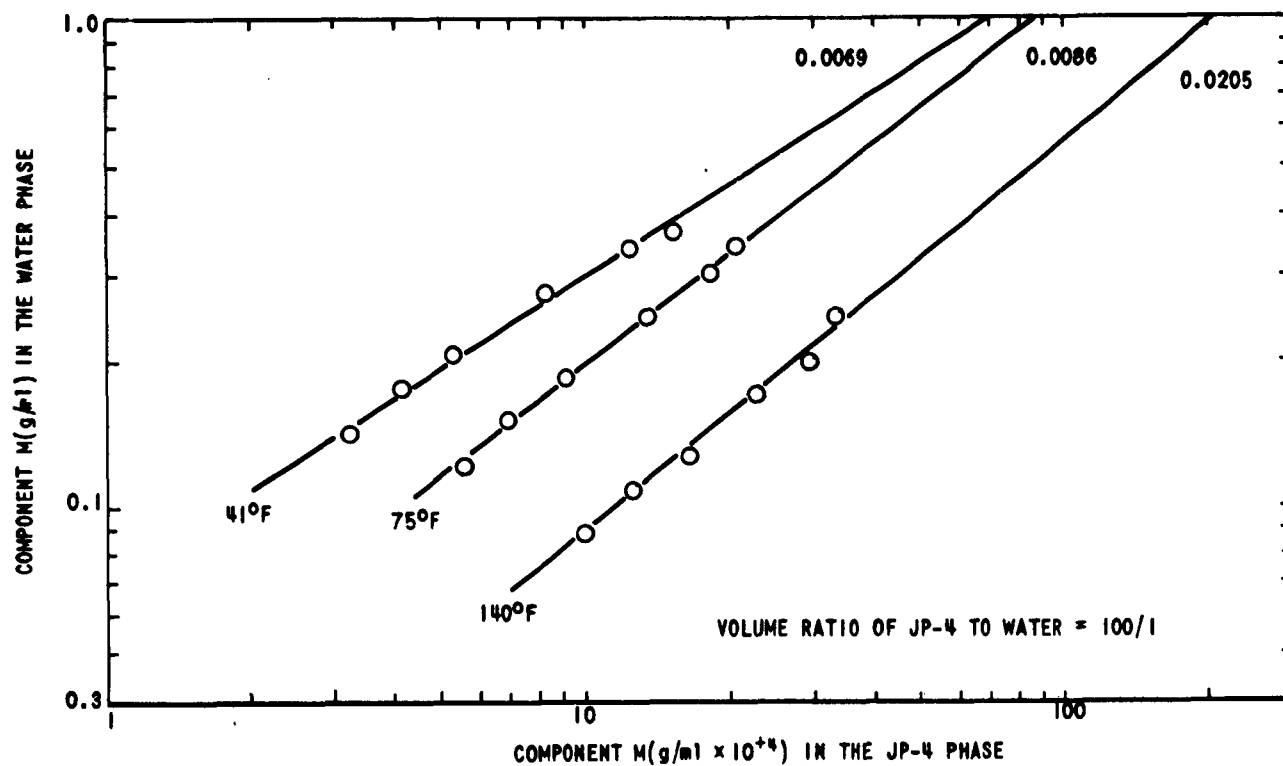
Fig. 12 - Distribution of Component M of P55MB Anti-Icing Additive in
JP-4 Jet Fuel and Water
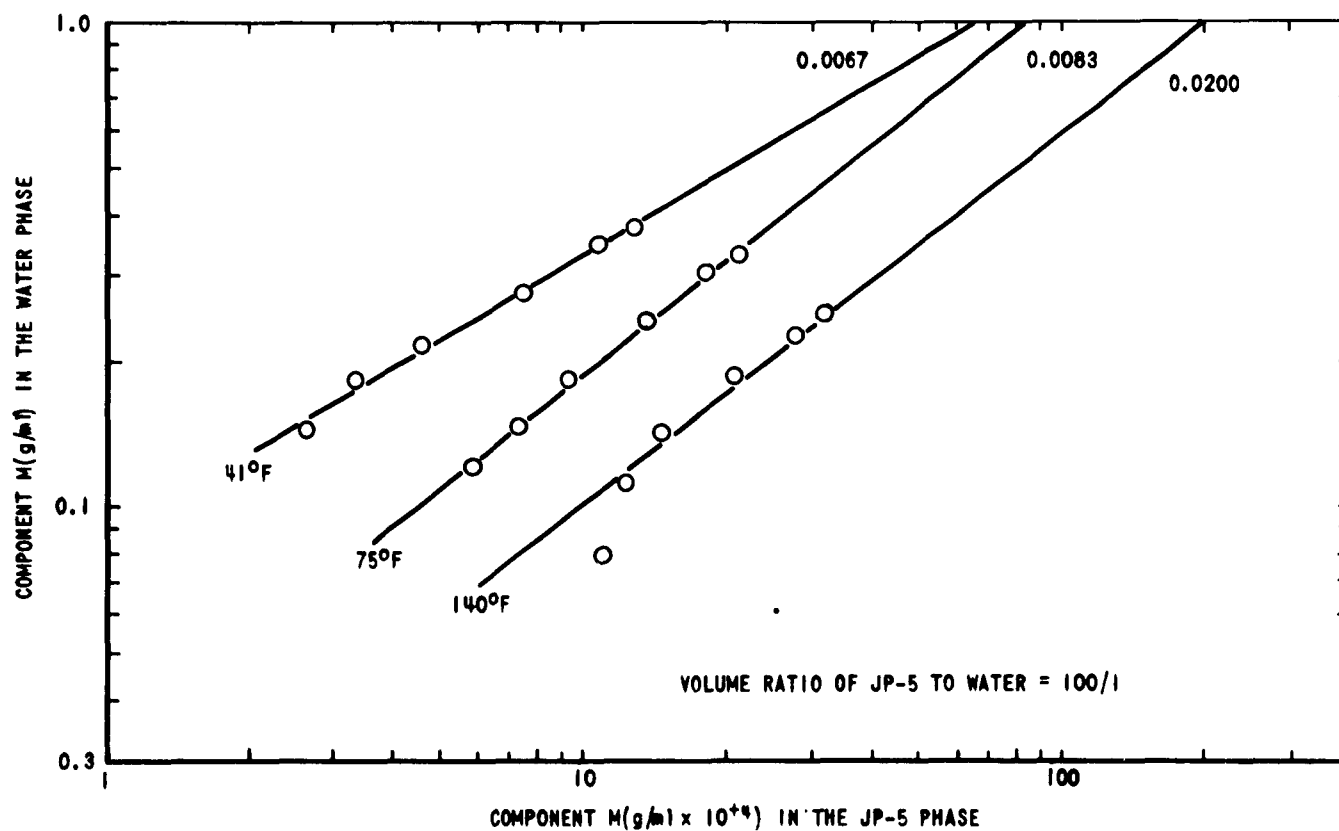
Fig. 13 - Distribution of Component M of P55MB Anti-Icing Additive in
JP-5 Jet Fuel and Water

Since the partition coefficient is a function of the concentration of Component M in the water phase, the slope of the straight lines shown in Figs. 12 and 13 must be known. The reciprocal of the value of each slope is equal to the exponent given in the following equation:

$$K = \frac{[M]^S_{H_2O}}{[M]_{JP}}$$

where

K = partition coefficient,

$[M]_{H_2O}$ = amount of Component M in the water phase,

$[M]_{JP}$ = amount of Component M in the fuel phase, and

S = reciprocal of the slope of line given in Figs. 12 and 13.

Since the partition coefficient and the value for the exponents are known, the amount of Component M extracted into the water from the fuel phase can be calculated.

The amount of association of Component M of P55MB in jet fuel and water is a function of temperature. This process of association of Component M is indicated by the change of the value for the exponent "S" given in the partition coefficient equation. Figure 14 gives the value of "S" as a function of temperature. The log value of "S" is plotted to reduce the curvature of the line.

Figure 15 gives the partition coefficient as a function of temperature for Component M of P55MB between jet fuels and water.

The maximum amount of P55MB which can be extracted into the water phase at a given temperature is shown in Fig. 16 for given additive concentrations in either JP-4 or JP-5 jet fuel. The volume ratio of jet fuel to water will determine the number of extractions necessary to reach maximum buildup in the water phase.

As the temperature is lowered, the maximum amount of additive in the water phase increases (see Fig. 16). This increase is not linear with temperature.
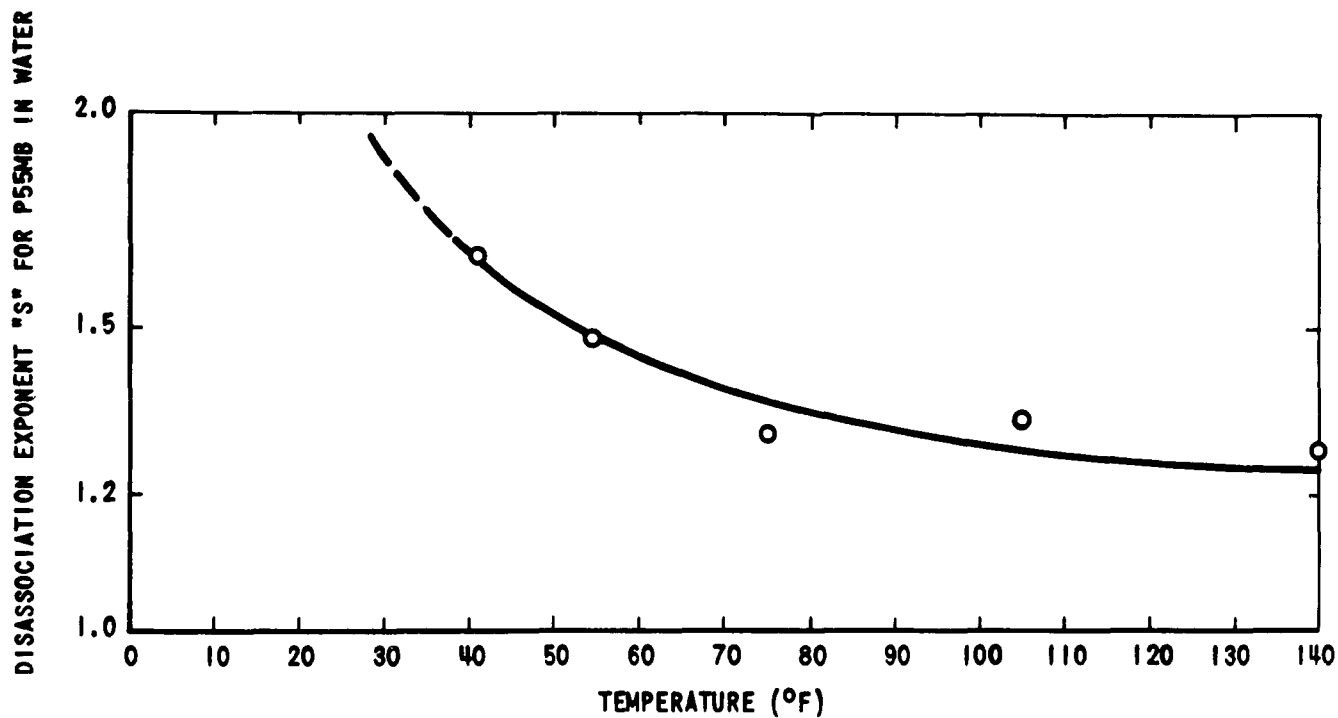
Fig. 14 - Dissociation Exponent "S" for P55MB in
Water as a Function of Temperature
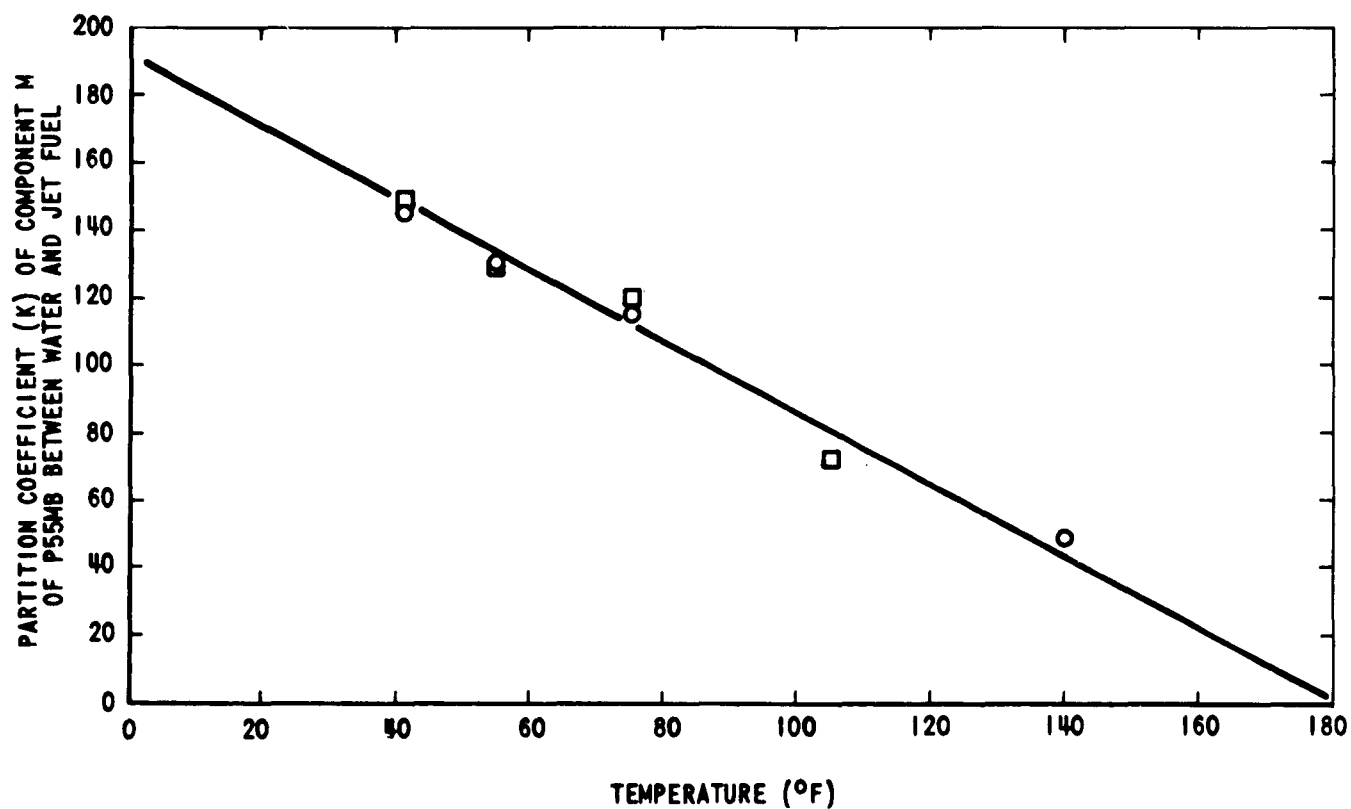
Fig. 15 - Partition Coefficient for Component M
of P55MB as a Function of Temperature
□ JP-5 Jet Fuel O JP-4 Jet Fuel
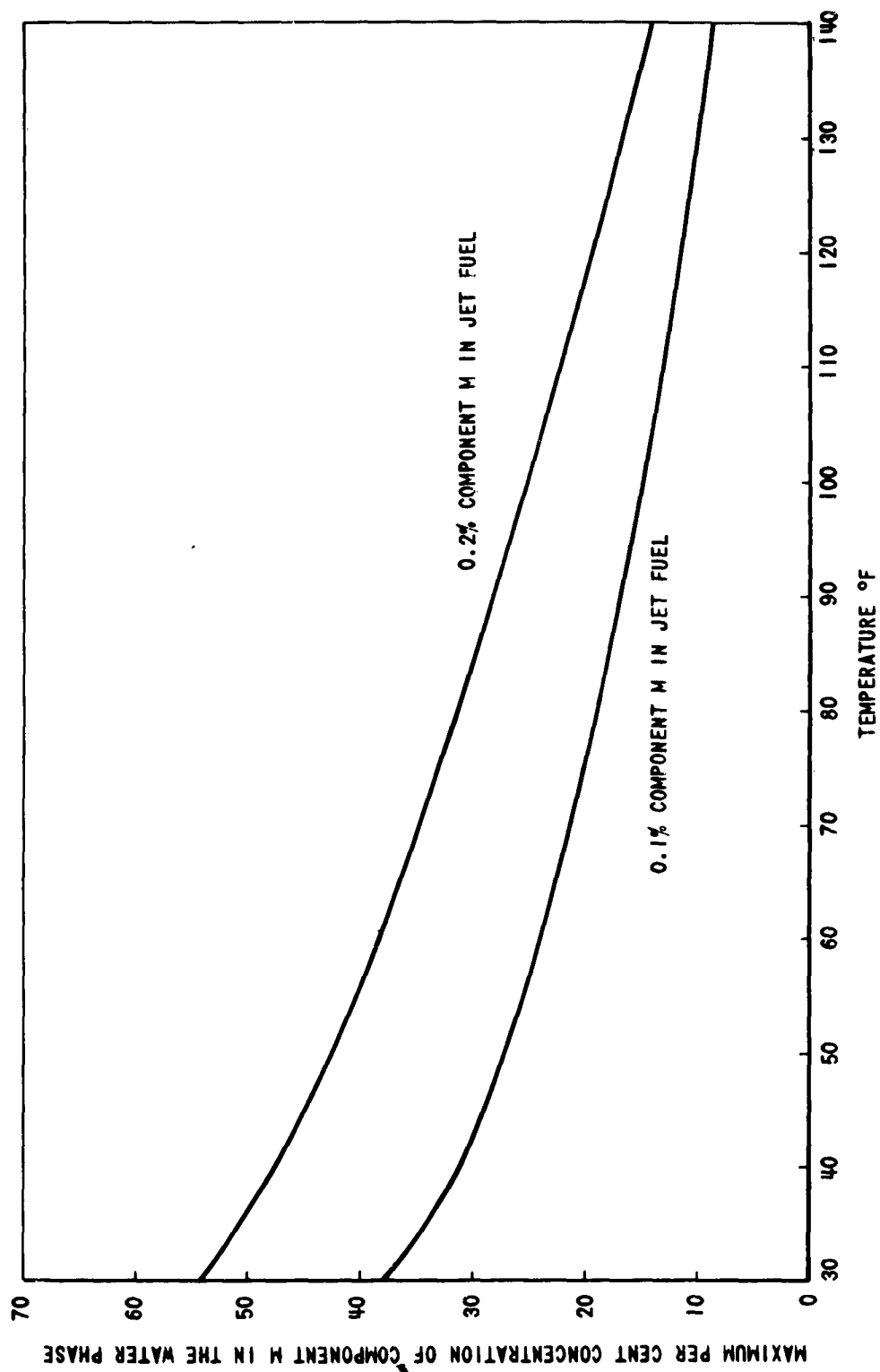
Fig. 16 - Maximum Buildup of Component M of P55MB in the Water Phase as a Function of Temperature

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2. Solubility of P55MB Anti-Icing Additive in Jet Fuel

The per cent solubility of P55MB in JP-4 and JP-5 jet fuels was determined at seven temperatures (-63, -33, -3, +41, +81, +105, and +140°F).

To each of seven containers, 10 ml. of additive was added to 50 ml. of jet fuel saturated at room temperature with water. The additive-fuel blends were shaken initially before they were placed into their respective constant temperature chambers and were shaken at intervals during a 24-hr. period.

After 24 hr., aliquots of the fuel were removed and the amount of P55MB was determined by Phillips Petroleum Company's analytical procedure for the determination of additive in jet fuel. Figure 17 shows the solubility of P55MB in JP-4 and JP-5 jet fuels as a function of temperature.

In both fuels, the solubility of P55MB at -65°F is greater than 0.3 per cent, indicating that at least 0.2 per cent additive will remain in the fuel to a temperature as low as -65°F. Experiments were performed to check the validity of the above results. Fuel samples containing 0.089 per cent P55MB were placed into each of seven control temperature chambers. After thermal equilibrium was established, aliquots of fuel were removed and analyzed for the presence of P55MB. At every temperature tested from 140 to -65°F the concentration of P55MB remained constant.

3. "Coupling Effect" Between Component M and Component G

Before the "coupling effect" could be measured, a procedure to analyze for the presence of small quantities of Component G had to be developed.

K. Furst,[2] describes a microanalytical method which uses 2,7-naphthalenediol for the determination of Component G. This method is much simpler and more accurate than the procedure outlined by Phillips Petroleum Company. Component M interferes with the test, but the interference can be nearly eliminated if an appropriate calibration curve is used.

The analytical procedure for the determination of Component G in jet fuel is as follows:

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[2] Furst, K., Mikro Chemie ver Mickrochim, Acta. 34, 25 (1948).
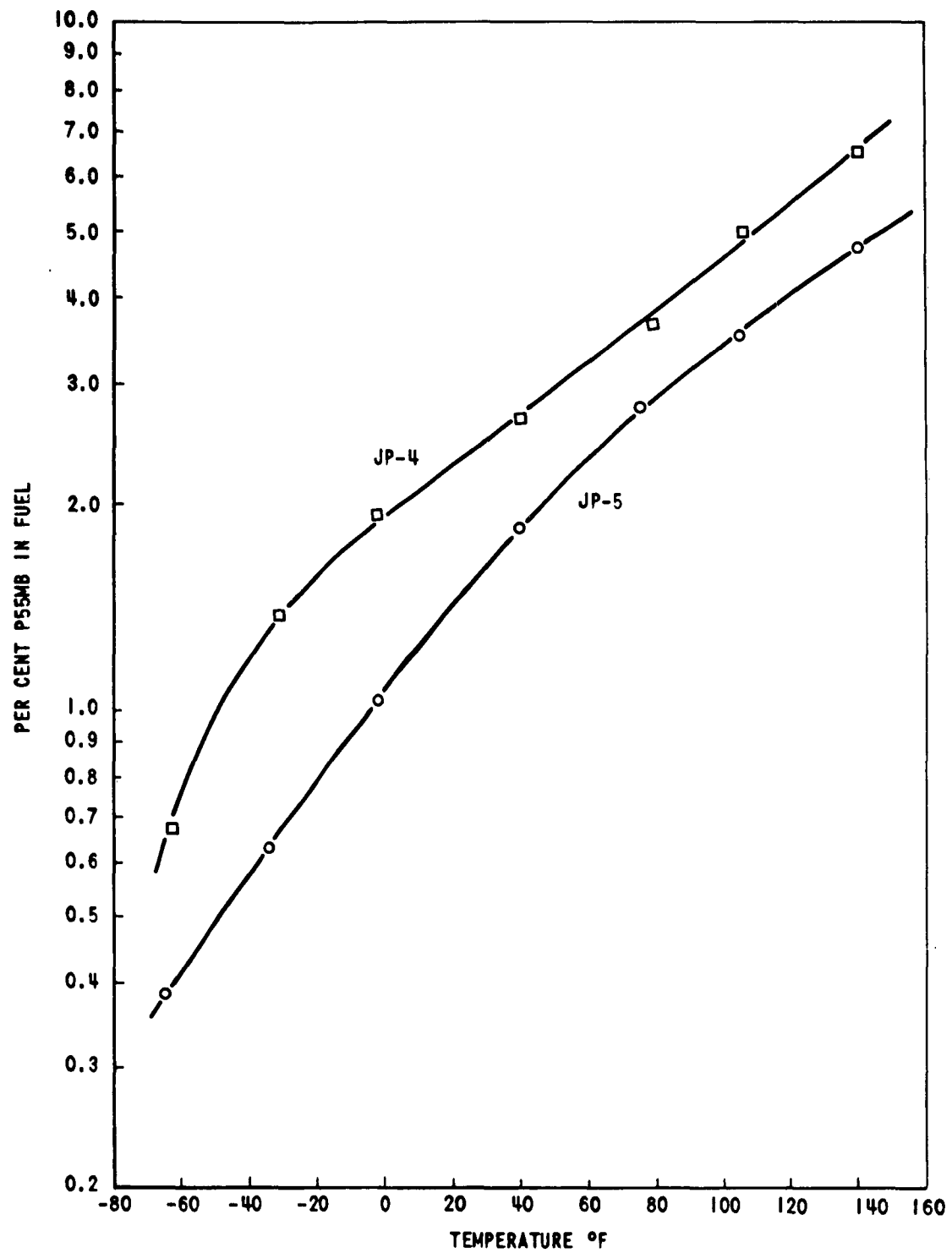
Fig. 17 - Solubility of P55MB in Jet Fuel

The additive is extracted from a 25-ml. aliquot sample of jet fuel by 2 min. shaking. The water phase is removed and a 1-ml. aliquot water extract sample is placed into a large test tube and cooled in an ice bath. Twenty milliliters of concentrated sulfuric acid is added to the sample along with 10 ml. of dye solution. The concentration of the dye solution is 0.0125 g. of 2,7-naphthalenediol per 500 ml. of concentrated sulfuric acid.

The sample, sulfuric acid, and dye solution are mixed well, stoppered, placed into a boiling water bath for 30 min., and then cooled to room temperature. A 20-ml. aliquot is pipetted into a 40-mm. rectangular cuvette and the fluorescence recorded with an appropriate spectrophotometer. The instrument used for experiments in this report was the Coleman Model 11 Universal Spectrophotometer.

The concentration of Component G is determined from a calibration curve of per cent transmission versus per cent Component G in water previously constructed using known concentrations of Component G in water.

Corrections for the presence of Component M are made by constructing a family of calibration curves using known concentrations of Component M in the presence of known concentrations of Component G in water.

If 0.1 per cent of additive in 25 ml. of fuel is extracted into 10 ml. of water, the total concentration of Component M in water will equal 0.225 per cent. Calibration curves obtained for the experiments described below were determined in the absence and in the presence of 0.2 per cent Component M.

In an effort to determine the "coupling effect", the solubilities of Component M and Component G in jet fuel were determined by the methods described in Section III, B, 2 and 3, p. 29. The solubility of Component M alone is greater than the solubility of the additive P55MB. Also, the solubility of Component G of P55MB is greater than the solubility of pure Component G in jet fuel. Figures 18 and 19 give the per cent solubility of Component M, and Component M of P55MB; and, Component G of P55MB and Component G in saturated jet fuel as a function of temperature, respectively.

4. Effects of P55MB on the Sedimentation Rate of Dispersed Droplet of Water in JP-4 Jet Fuel

JP-4 jet fuel was saturated with water at 140°F. As the sample cooled to room temperature (75°F), dispersed micro-droplets of water formed

Fig. 19 - Solubility of Component G and Component G
Content of P55MB in JP-4 Jet Fuel as a
Function of Temperature

Fig. 18 - Solubility of Component M and Component M
Content P55MB in JP-4 Jet Fuel as a
Function of Temperature

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in the fuel. The initial increase in turbidity followed by a continuous de-
crease in turbidity was recorded as the per cent transmission of light through
a 40-mm. cuvette. The transmission of light was measured using a Coleman
spectrophotometer. The decreasing rate of change in the turbidity was assumed
to be directly related to the sedimentation rate of the dispersed droplets of
water.

The above experiment was repeated with the exception that P55MB was
added to jet fuel supersaturated with water. The additive concentration in
the fuel was 0.2 per cent. Figure 20 shows the per cent transmission as a
function of time for JP-4 jet fuel with and without additive P55MB. The
minimum in each curve on Fig. 20 represents the maximum turbidity of the fuel
sample. The sedimentation rate is represented by the straight line drawn
tangent to the increase in transmission.

IV. EFFECTS OF P55MB AND ADDITIVE "A" ON THE FUEL-TANK TOPCOATING

A. Discussion of Results and Conclusions

Although many anti-icing additives have been found, very few of
them are compatible with the Buna-N phenolic resin used as a fuel-tank top-
coating in jet aircraft.

Phillips anti-icing additive P55MB has been flight tested, and
preliminary compatibility studies made. Additive "A" has been found from
laboratory experiments to be a good anti-icing additive, and preliminary
laboratory experiments indicated that it was compatible with the fuel-tank
topcoating.

More exhaustive compatibility experiments were performed with P55MB
and Additive "A" anti-icing additives.

Compatibility studies have indicated that the fuel-tank topcoating
is more resistant to an attack by JP-5 fuel alone than to an attack by JP-4
jet fuel. However, if the fuels contain P55MB, the maximum concentration
that can be in the fuel before serious solubilization of the resin will occur
is 0.6 per cent (see Figs. 21 and 23, pp. 38 and 39).
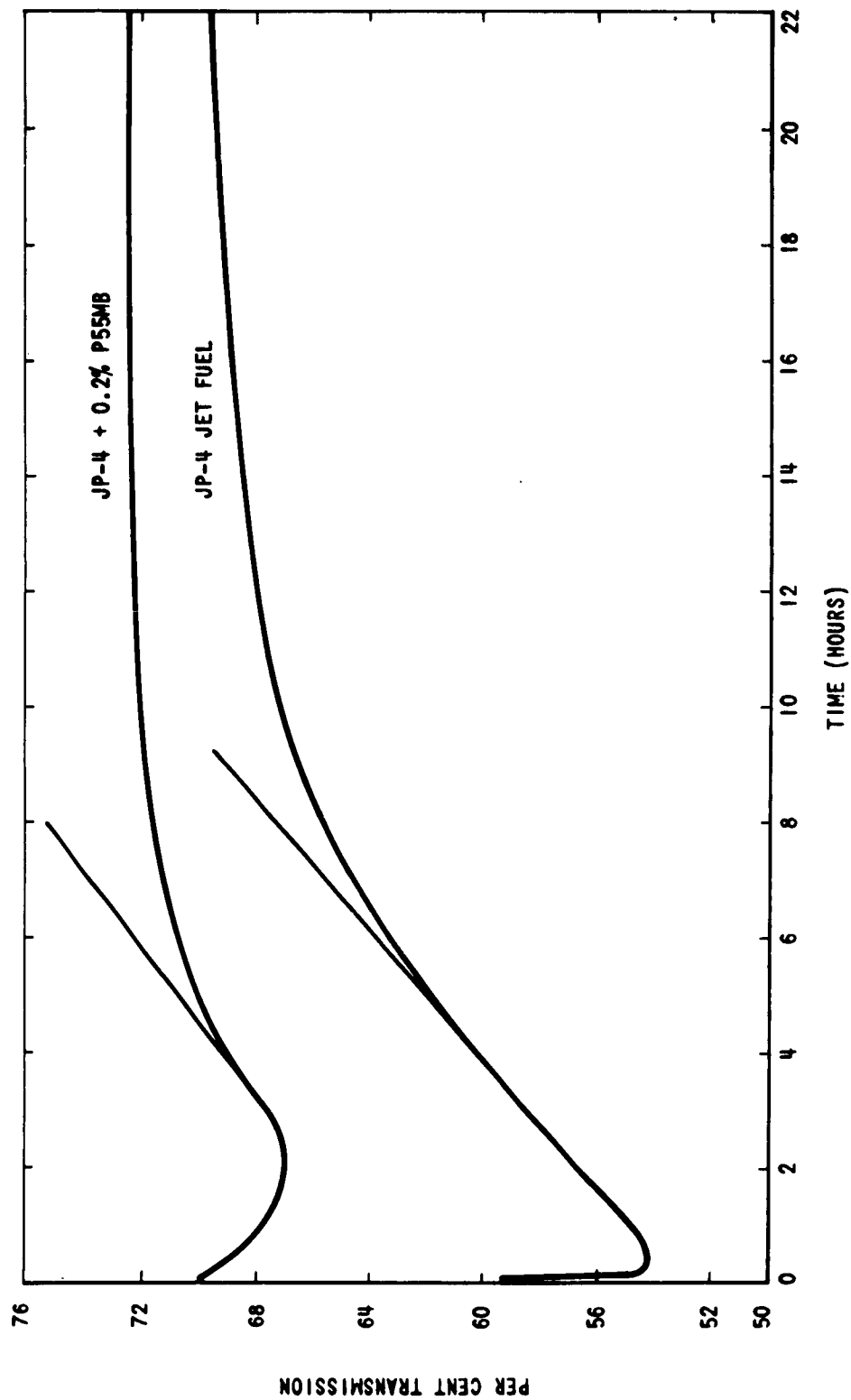
Fig. 20 - Sedimentation Rate of Dispersed Droplet of Water With
and Without P55MB in JP-4 Jet Fuel

If the additive in the fuels is Additive "A", no maximum concentration of the additive can be obtained below which no serious solubilization takes place. The resistance of the fuel-tank topcoating decreases linearly with the concentration of Additive "A" in the fuel phase (see Figs. 22, 24, and 25, pp. 38, 39, and 40).

As in JP-4 jet-fuel data previously published, the fuel-tank topcoating increases in hardness with increasing exposure time to the P55MB-JP-5 jet fuel mixture. This increase in hardness will occur only if the concentration of the additive is 0.6 per cent or less. As in the case of JP-4 jet fuel, there is an initial softening of the resin with JP-5 containing P55MB anti-icing additive for a short time. Recovery and further increase in hardness are noted as exposure time increases (Fig. 26, p. 42).

Additive "A" in JP-5 jet fuel will initially soften the fuel-tank topcoating and then allow it to recover over a given period of time. However, recovery does not exceed the initial hardness of the resin except when the concentration is equal to 0.2 per cent. No recovery of the resin hardness, after 168 hr., occurs when Additive "A" is used in JP-4 jet fuel (see Figs. 27 and 28, pp. 42 and 43).

Additive "A" in the water phase attacks the fuel-tank topcoating to a greater degree than does P55MB of the same concentration. Not only softening of the resin occurred, but blistering was noted after 24 hr. (Fig. 30, p. 44).

On the basis of the statements made above, it can be concluded that Additive "A", although a good anti-icing agent, will not be compatible with the fuel-tank topcoating even though preliminary experiments indicated it to be.

Further experiments were performed on P55MB to determine what effects the ratio of Component M to Component G would have on the hardness of the Buna-N phenolic resin. The ratios used were 60/40, 70/30, 80/20, and 95/5. One-half of 1 per cent (0.5) of the various ratios in JP-4 and JP-5 jet fuels showed little difference from 0.5 per cent P55MB concentrations in the fuels after 168 hr. at 140°F (see Figs. 32 and 33, pp. 45 and 46).

On the other hand, Component G in the water phase tends to increase the resistance of the fuel tank topcoating to attack by water. This effect is shown in Fig. 34, p. 46. Also, shown for comparison is a 1 per cent solution of P55MB in water for the same length of time.

Since the ratio of Component M to Component G in the fuel phase does not affect the resin, and increasing Component G in the water phase will prevent Component M and water from attacking the topcoating, the ratio of Component M to Component G should be of such a value that the maximum solubility of Component G in the fuel is obtained when 0.1 per cent additive concentration is used. Therefore, in the presence of water, Component G will be extracted from the fuel so that a maximum concentration would be obtained in the water phase. The higher the concentration of Component G in the water phase, the less the attack of the topcoating by water and P55MB. A study is also recommended of the feasibility of flushing the fuel tank and filling the sump with Component G before fueling a jet aircraft.

The effects on the fuel-tank topcoating of cycling the temperature of the fuel-additive mixtures between +140 and -65°F were studied (see Table III, Section IV, B, 1, p. 48). The results, although not conclusive, indicate that the two additives, P55MB and Additive "A" (in JP-4 and JP-5 fuels), affect the topcoating more when the temperature is cycled than if the temperature remains constant. This trend may be explained by the limited solubility of the additives in the fuels at extremely low temperatures.

Compatibility studies of P55MB were performed on scaled-down fuel tanks supplied by Boeing Airplane Company. Tests were run to determine the effects of cycling the temperature from +140°F to -65°F on the topcoating of the tanks. Table IV, p. 49, lists the results. Very little change in the topcoating hardness and appearance was noted after the first month of cycling the temperature. However, during the first month softening of the resin occurred, and the dye was leached from the resin.

The methods for testing compatibility in the laboratory and in the field differ. The laboratory method is the Sward Rocker Hardness Test, which relates the hardness of any materials to the hardness of plate glass. Since it is not feasible to use the Sward Rocker in the field to test the hardness of the topcoating already present in the fuel tanks of an aircraft, the Pencil Hardness Test is used.

To compare laboratory data with the field data, the two test procedures must be correlated. Figure 35, p. 47, shows the nearly linear relationship between the Pencil Hardness and Sward Hardness when the EC 776-SR resin is drying. But when the resin is softened by a solvent (water), the relationship between the Pencil Hardness and Sward Hardness Tests changes and does not approach linearity. Therefore, before any laboratory test can be correlated with the field test, the history of the resin must be known.

B. Experimental

1. Compatibility Studies of P55MB and Additive "A" Anti-Icing Additives

The preparation of the aluminum test panels which were used in the compatibility studies and the evaluation of the change in compatibility is given below.

Alclad aluminum panels (3 in. x 5 in.), relatively free of any scratch marks, were cleaned with a mixture of 50 per cent toluene, 20 per cent ethyl acetate, 20 per cent methyl ethyl ketone, and 10 per cent isopropyl alcohol. After being cleaned, the panels were dried and stored until ready for use.

The procedure used for coating test panels with the Buna-N phenolic resin differs from the dip-coating method used by ASD. It is essential that the resin be of uniform thickness on the aluminum panel when the Sward Rocker Hardness Tester is used. By means of a doctor bar with 0.006 in. clearance, a reproducible thickness (approximately 0.002 in. dry film) of EC 776-SR resin 2 in. wide was coated on the aluminum panel. The resin was dried for 48 hr. at a constant temperature of 74°F.

The hardness of the test panels was measured before and after immersion in the test solutions with a Sward Rocker Hardness Tester. The change in hardness of the Buna-N phenolic resin was computed in terms of per cent fuel-tank topcoating hardness change for initial value.

The effects of time of exposure and of the concentration of the two anti-icing additives, P55MB and Additive "A", in JP-4 and JP-5 jet fuels upon the surface hardness of the fuel-tank topcoating (a Buna-N phenolic resin) were determined at 140°F.

Figure 21 compares the effect upon the topcoating, under identical conditions, of P55MB in JP-5 fuel with that of its effect in JP-4 fuel. The latter data were published in WADD Technical Report 60-226, Part II, p. 35. Similarly, Fig. 22 compares the separate effects of Additive "A" upon the topcoating in both JP-4 and JP-5 jet fuels.

Figures 23 and 24 illustrate the individual effects upon the topcoating of various concentrations of both P55MB and Additive "A" in JP-5 jet fuel for given lengths of time at 140°F. Figure 25 is a graph of the effects of various Additive "A" concentrations in JP-4 fuel upon the topcoating for
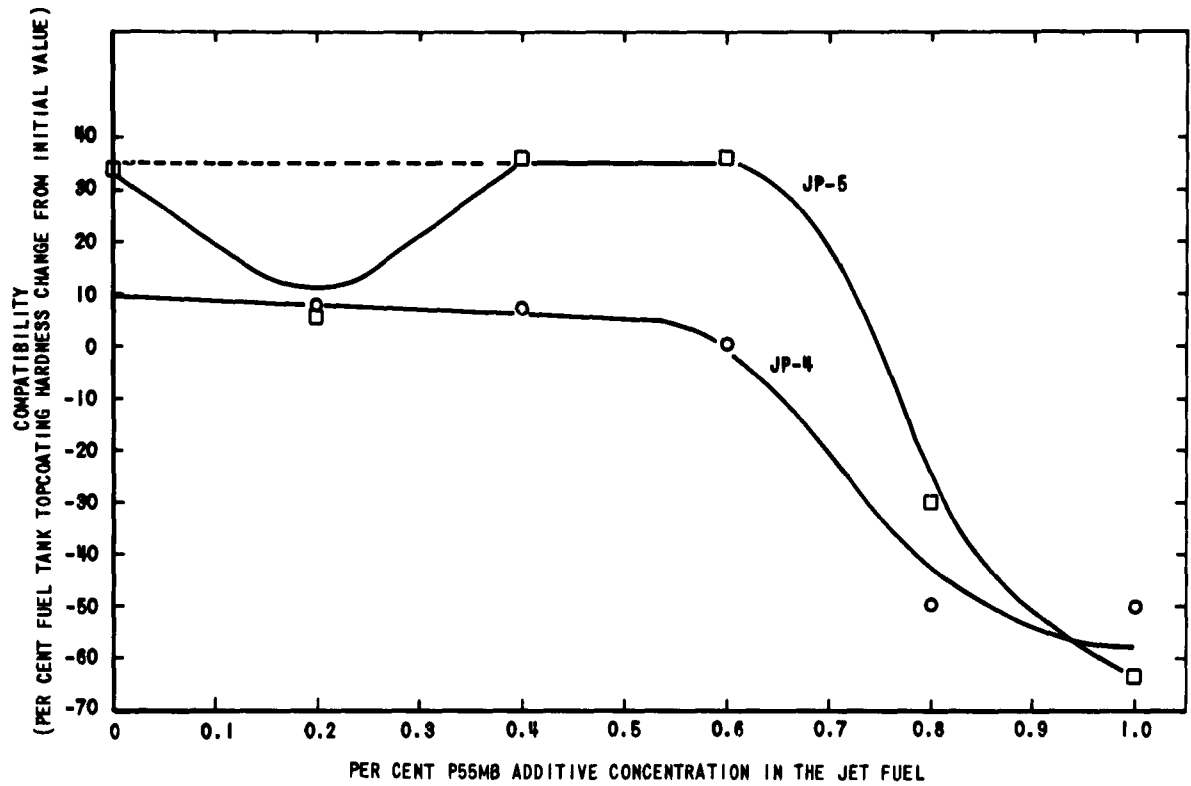
Fig. 21 - Comparison of the Fuel-Tank Topcoating Hardness as a Function
of P55MB Additive Concentration After 88 Hr. at 140°F in JP-5
Jet Fuel With That Previously Published for JP-4 Jet Fuel
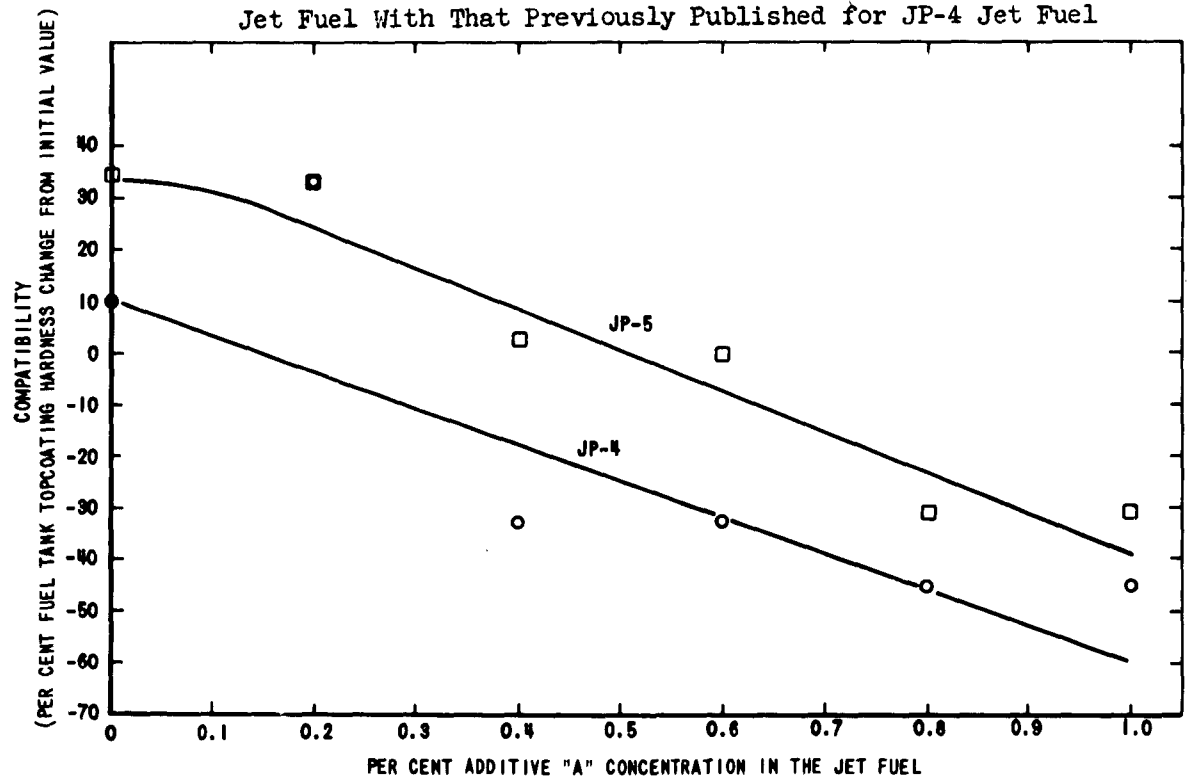
Fig. 22 - Fuel-Tank Topcoating Hardness as a Function of
Additive "A" Concentration After 88 Hr. at
140°F in JP-4 and JP-5 Jet Fuel

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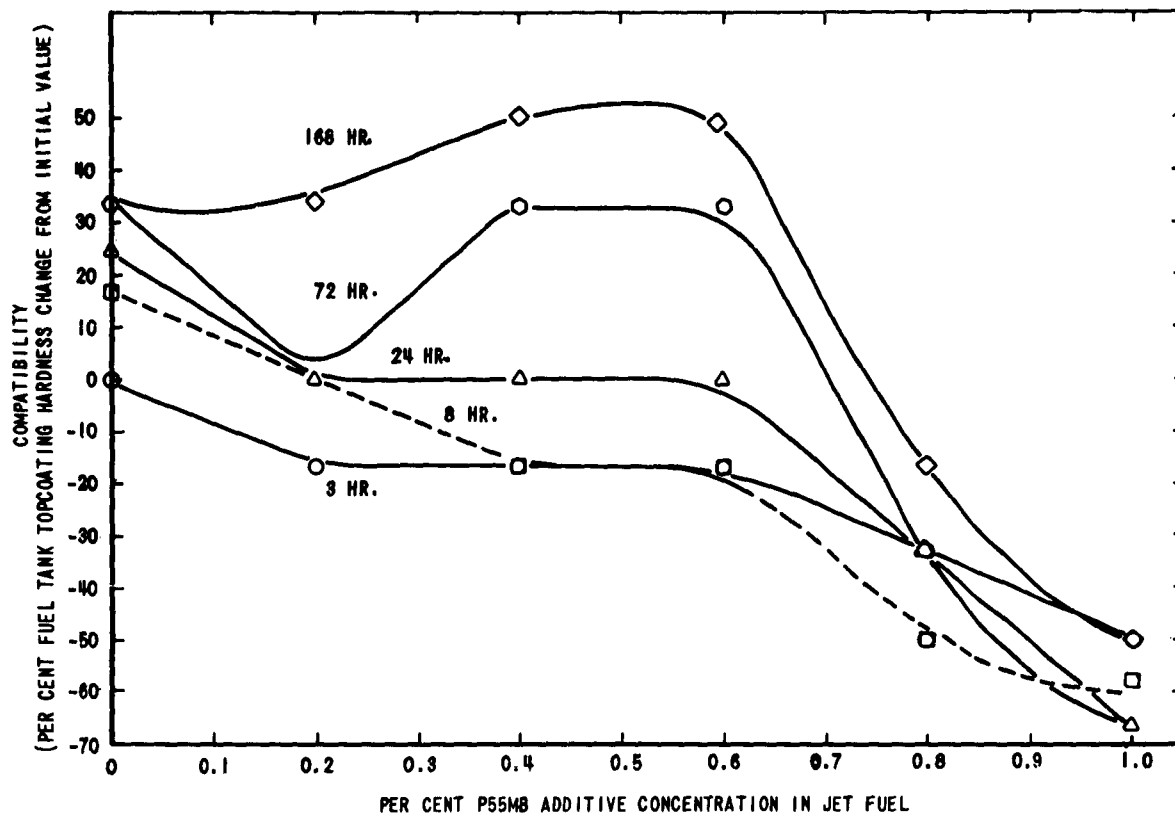
Fig. 23 - Fuel-Tank Topcoating Hardness as a Function of P55MB
Additive Concentration and Time at 140°F
in JP-5 Jet Fuel
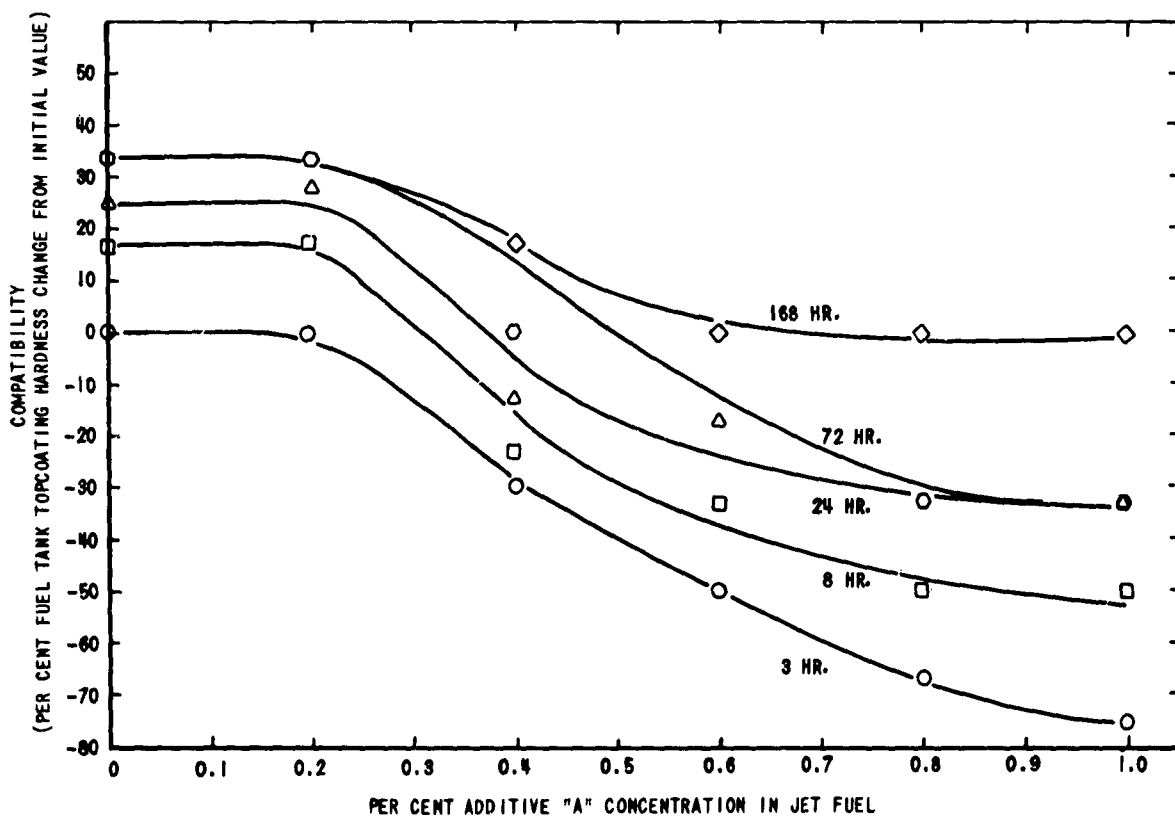
Fig. 24 - Fuel-Tank Topcoating Hardness as a Function of
Additive "A" Concentration and Time at 140°F
in JP-5 Jet Fuel
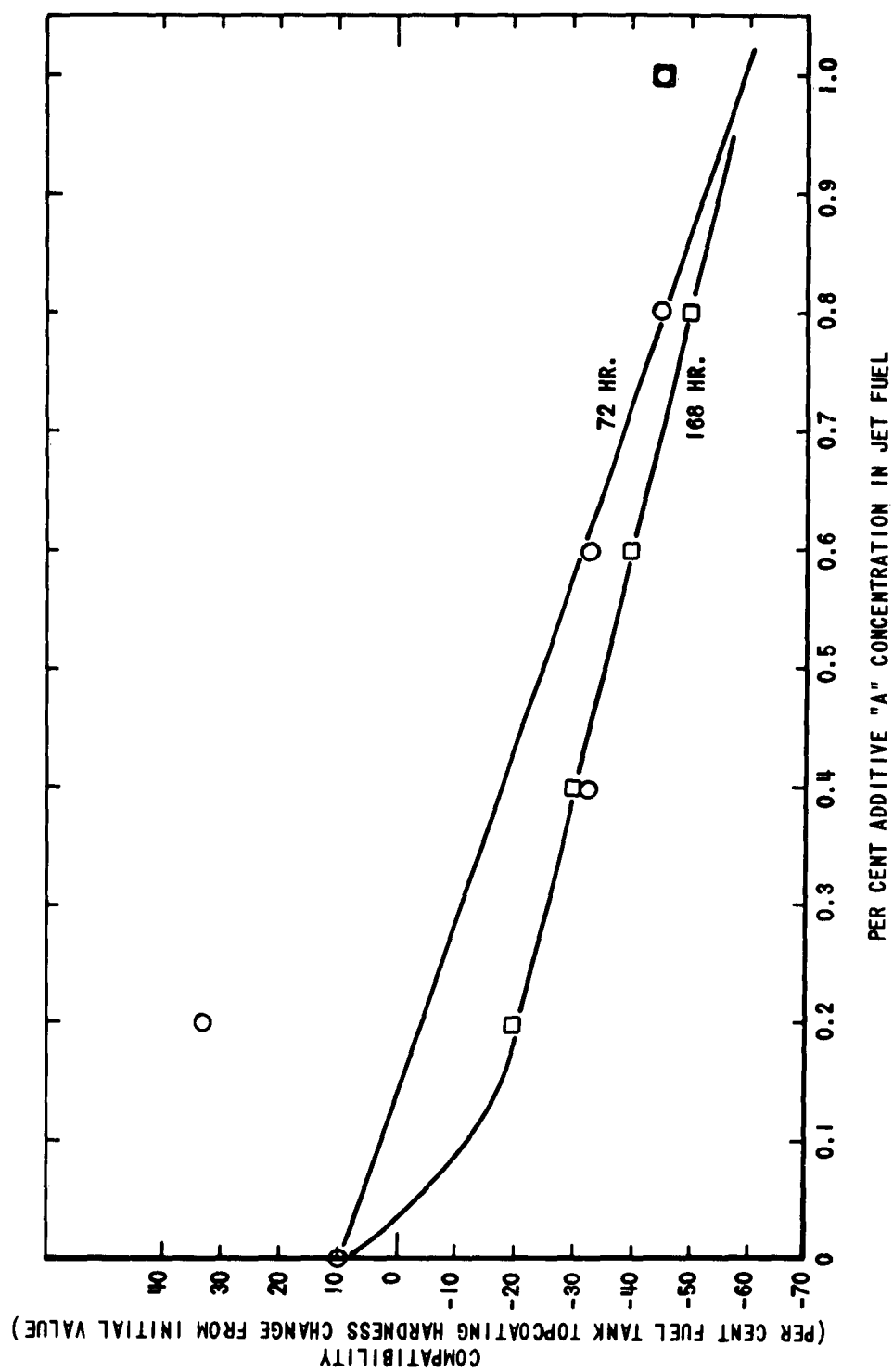
Fig. 25 - Fuel-Tank Topcoating Hardness as a Function of Additive "A" Concentration and Time at 140°F in JP-4 Jet Fuel

72 and 168 hr. exposure of the test panels at 140°F. Comparable data for P55MB in JP-4 are given on p. 35 of WADD Technical Report 60-226, Part II, and are reproduced in Fig. 29.

Figures 26 and 27 are replots of the data shown in Figs. 23 and 24, respectively, in which the additive concentrations and exposure times were exchanged on the abscissa axis. Similarly, Fig. 28 is a replot of Fig. 25. Comparable data for P55MB in JP-4 are given on p. 35 of WADD Technical Report 60-226, Part II, and are reproduced in Fig. 30.

Experiments were performed to determine the effect of various concentrations of P55MB and Additive "A" in water on the change in hardness of the Buna-N phenolic resin. Figure 31 compares the effects of the two anti-icing additives in water with water alone for an exposure time of 24 hr. at 140°F.

The optimum per cent of Component G in P55MB was determined by measuring the effect of various ratios of Component M to Component G upon the fuel-tank topcoating. The results for 0.5 per cent total additive concentration in both JP-4 and JP-5 fuels as a function of time at 140°F are given in Figs. 32 and 33, respectively.

To show that Component G acts as an inhibitor for the solubilizing effects of Component M on the fuel-tank topcoating in the water phase, the fraction of Component G in the water phase was increased from 10 to 40 per cent. Figure 34 shows the effect of 10, 20, and 40 per cent of Component G in the water phase to the effect of 1 per cent P55MB in water and water alone on the change in hardness of the fuel-tank topcoating.

Since jet fuels will be subjected to variation in temperature during flight, experiments were performed to determine the effect of cycling the temperature of the fuel-additive mixtures on the change in hardness of the fuel-tank topcoating.

Aluminum test panels were placed into solutions of P55MB and Additive "A", in both JP-4 and JP-5 jet fuels. The concentrations of each additive in each of the fuels were 0.1, 0.3, and 0.5 per cent.

The test panels in the solutions were subjected to a temperature of 140°F on alternate days, and were maintained at -65°F the remainder of the time. The total exposure time of the test panels was one week. Table III is a list of the results obtained, and provides a comparison of these results to the data on test panels not subjected to cycling of the temperature.
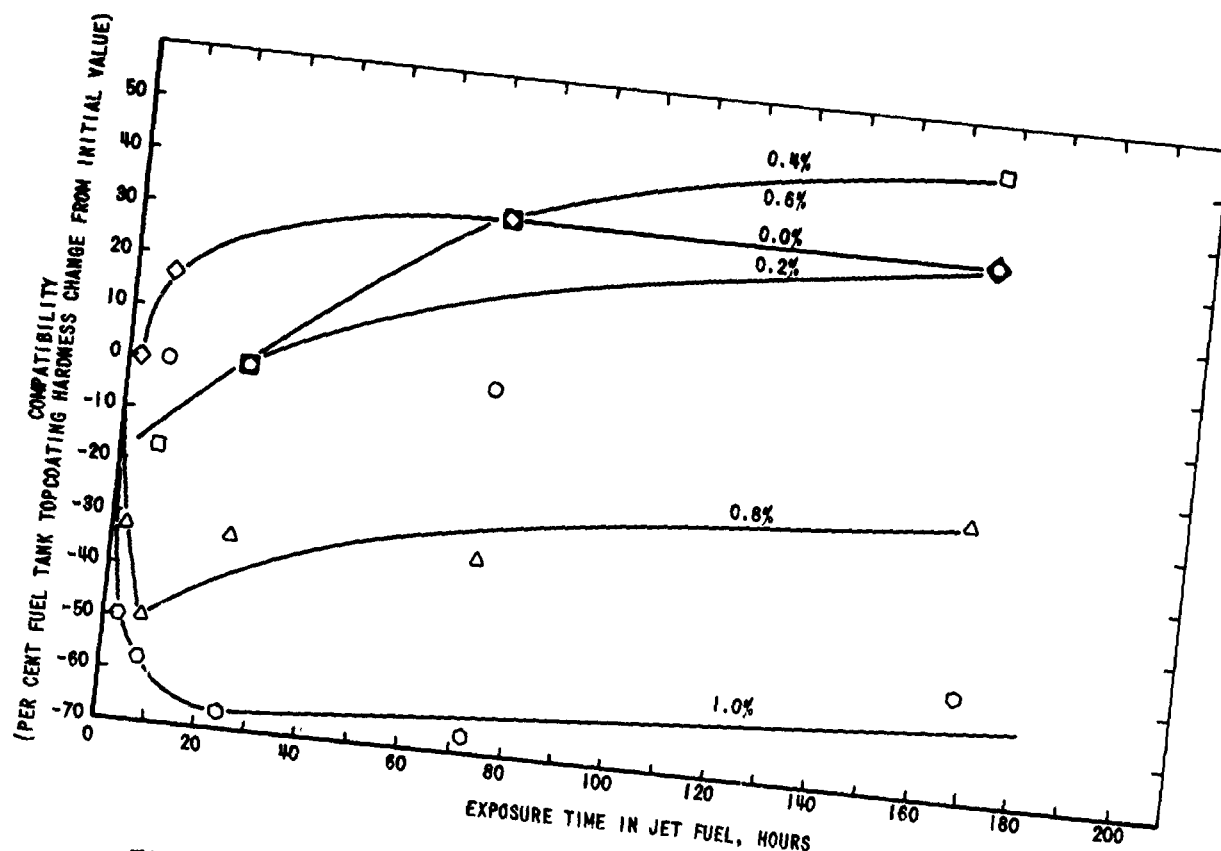
Fig. 26 - Fuel-Tank Topcoating Hardness as a Function of Time
at 140°F and P55MB Additive Concentration
in JP-5 Jet Fuel
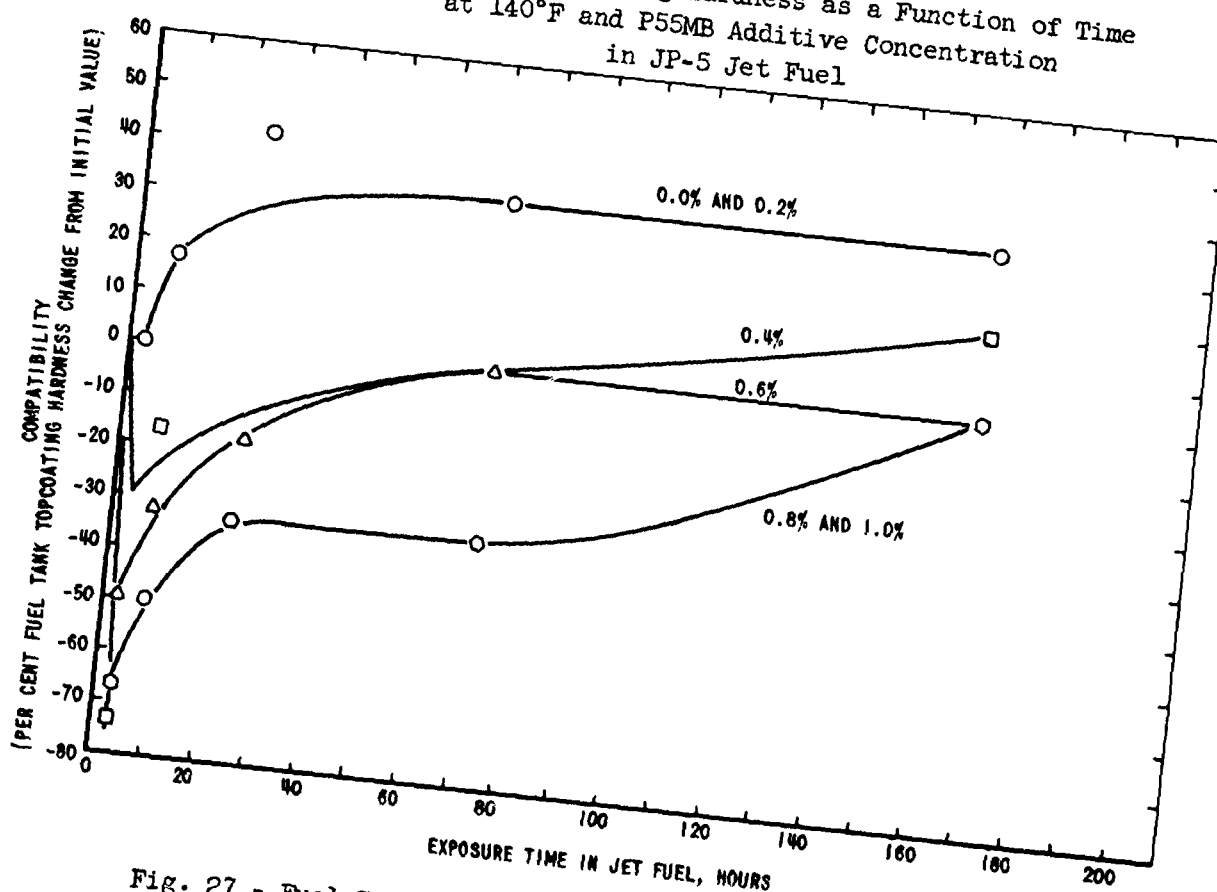
Fig. 27 - Fuel-Tank Topcoating Hardness as a Function of Time
at 140°F and Additive "A" Concentration
in JP-5 Jet Fuel
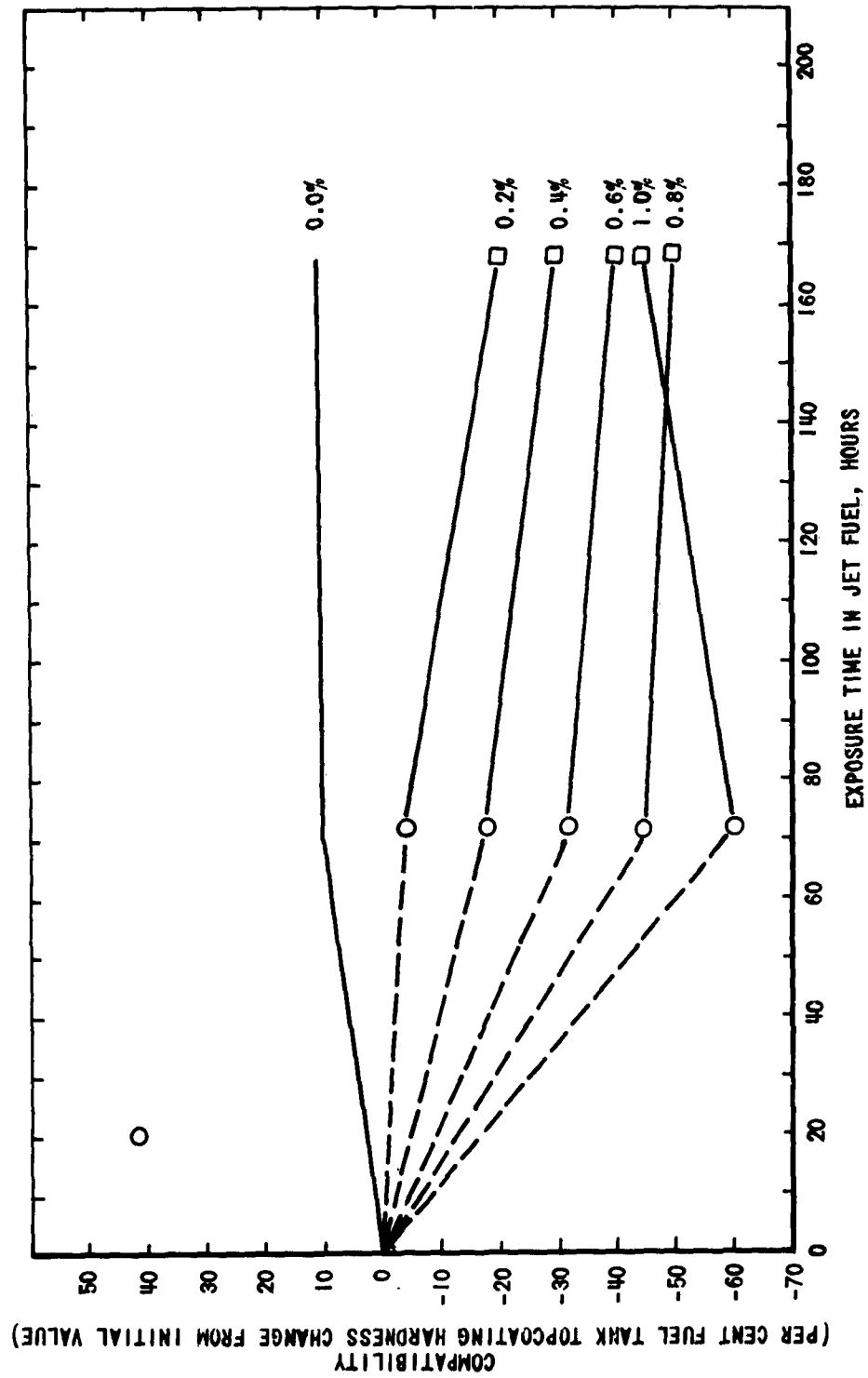
Fig. 28 - Fuel-Tank Topcoating Hardness as a Function of Time at 140°F and Additive "A" Concentration in JP-4 Jet Fuel
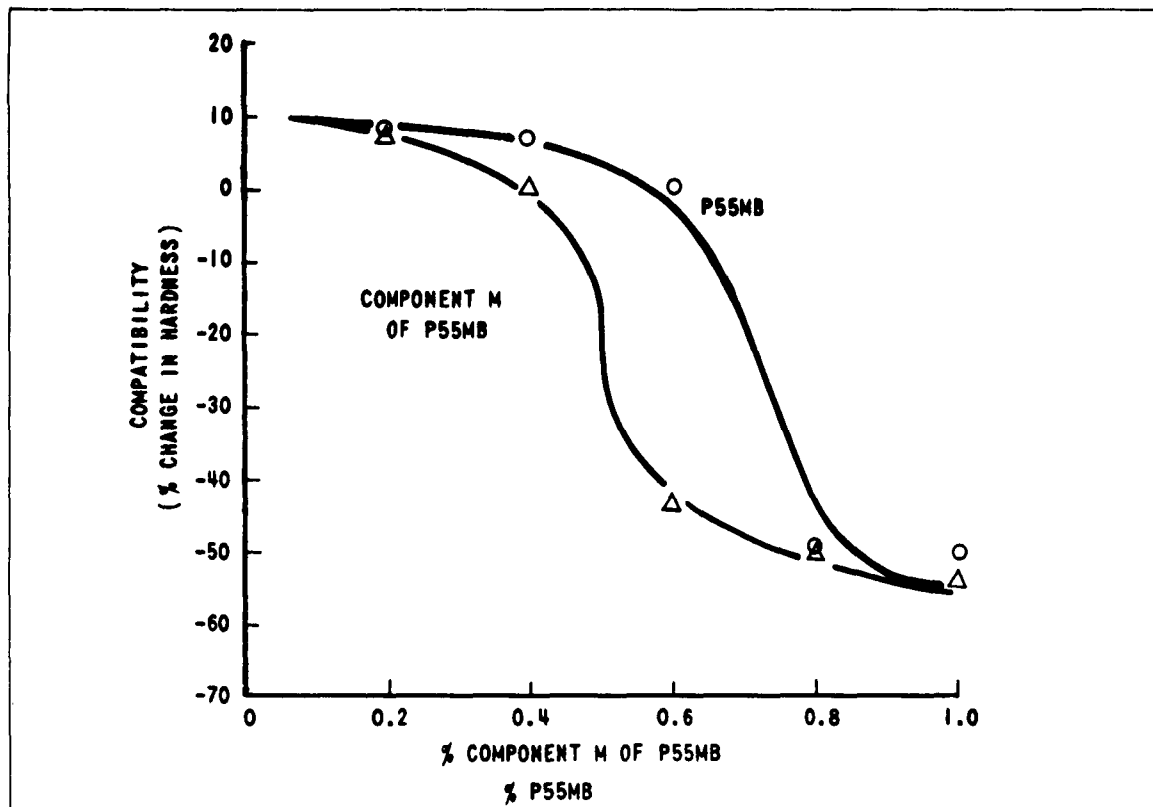
Fig. 29 - The Effects of the Modifier in P55MB on the
Compatibility of the Additive in JP-4 Fuel
(Exposure Time 88 Hr., Temperature 140°F)
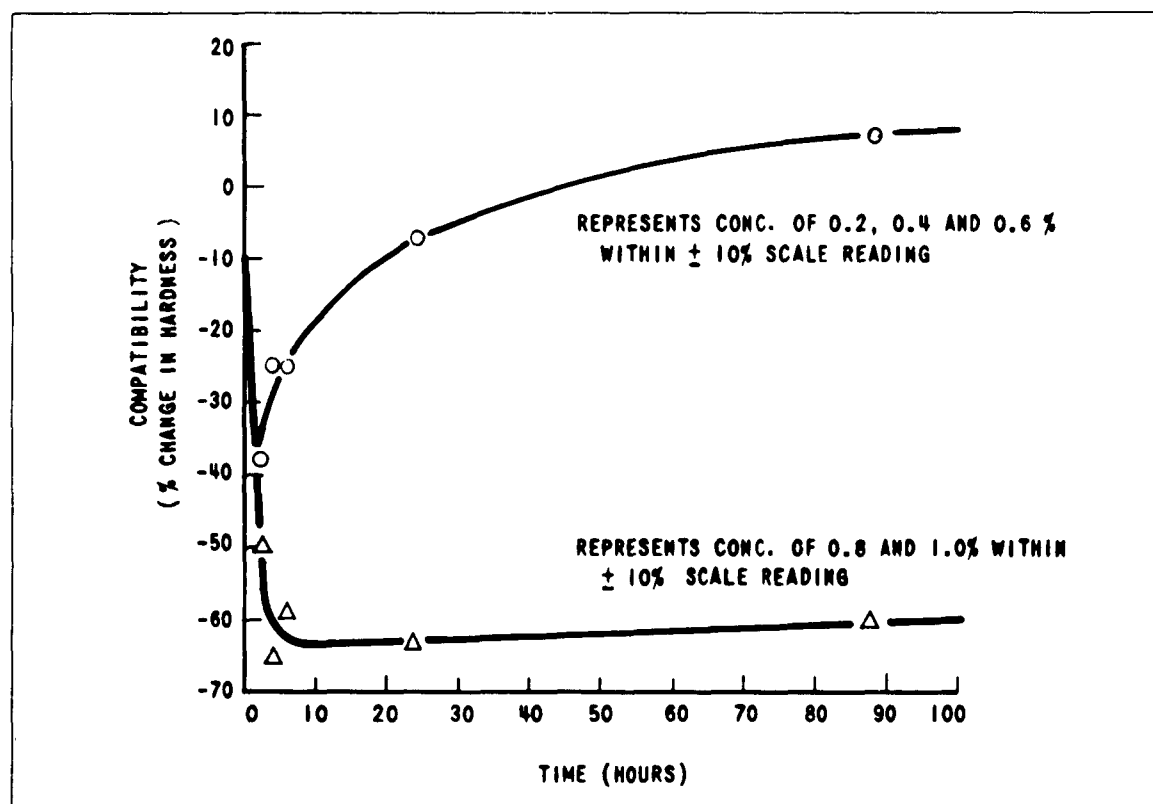
Fig. 30 - Compatibility Versus Exposure Time of Various
Concentrations of P55MB in JF-4
(Temperature 140°F)
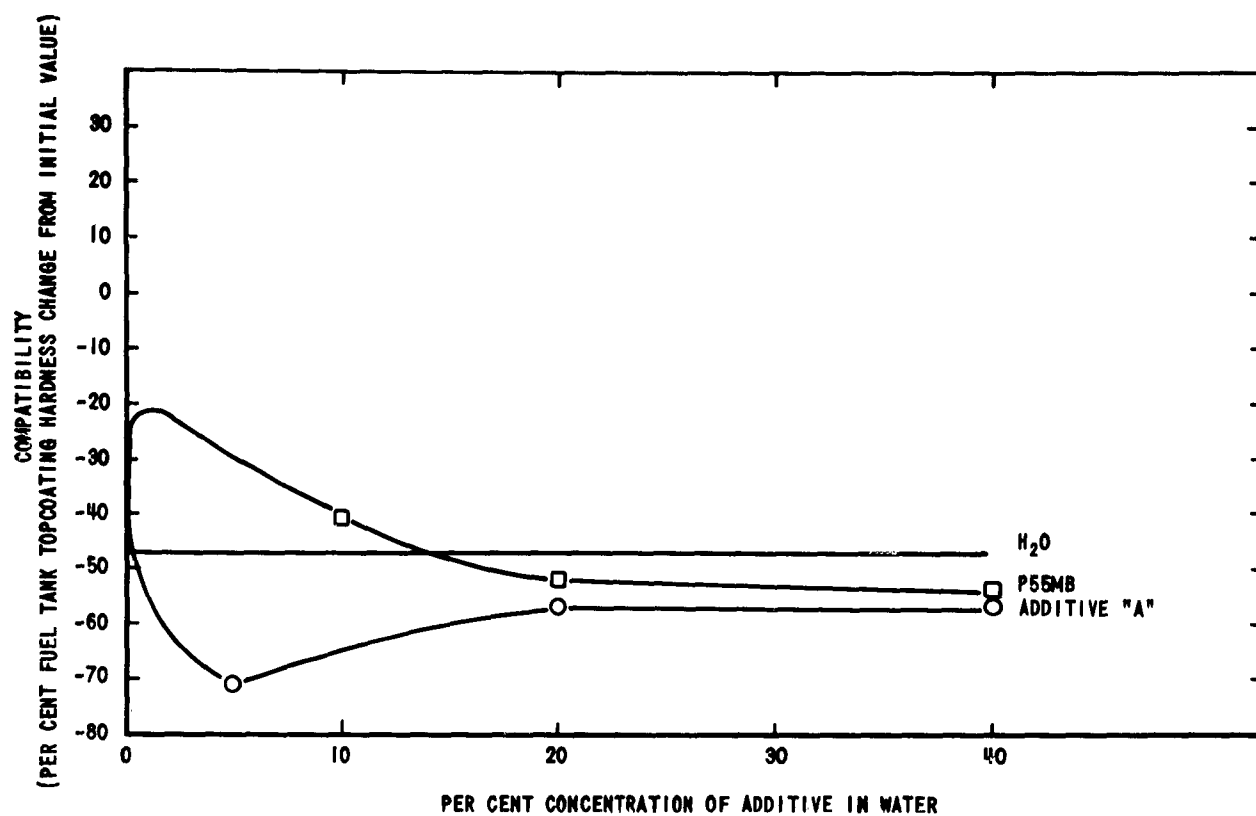
Fig. 31 - Fuel-Tank Topcoating Hardness as a Function of
Additive Concentration in Water
(24-Hr. Exposure at 140°F)
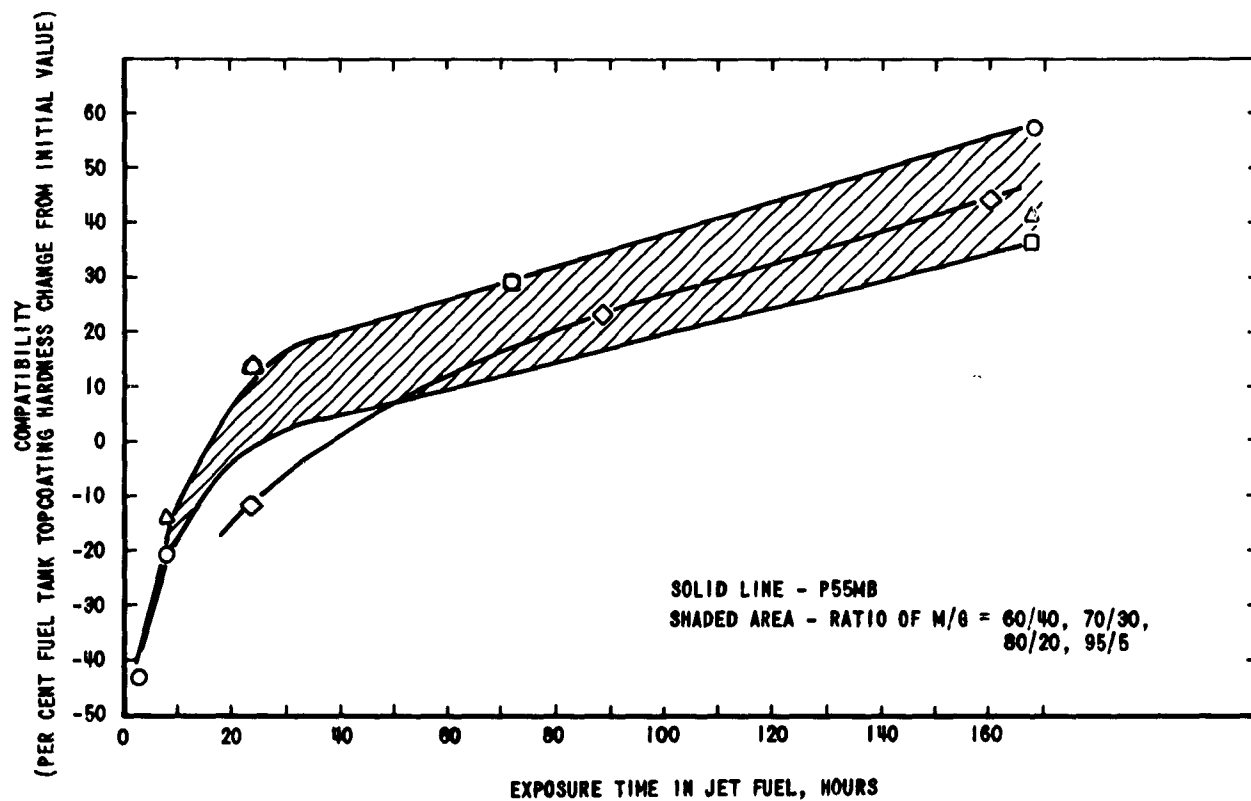
Fig. 32 - Fuel-Tank Topcoating Hardness as a Function of Time at
140°F and Ratio of P55MB Additive Components at 0.5
Per Cent Total Additive Concentration in JP-4 Fuel
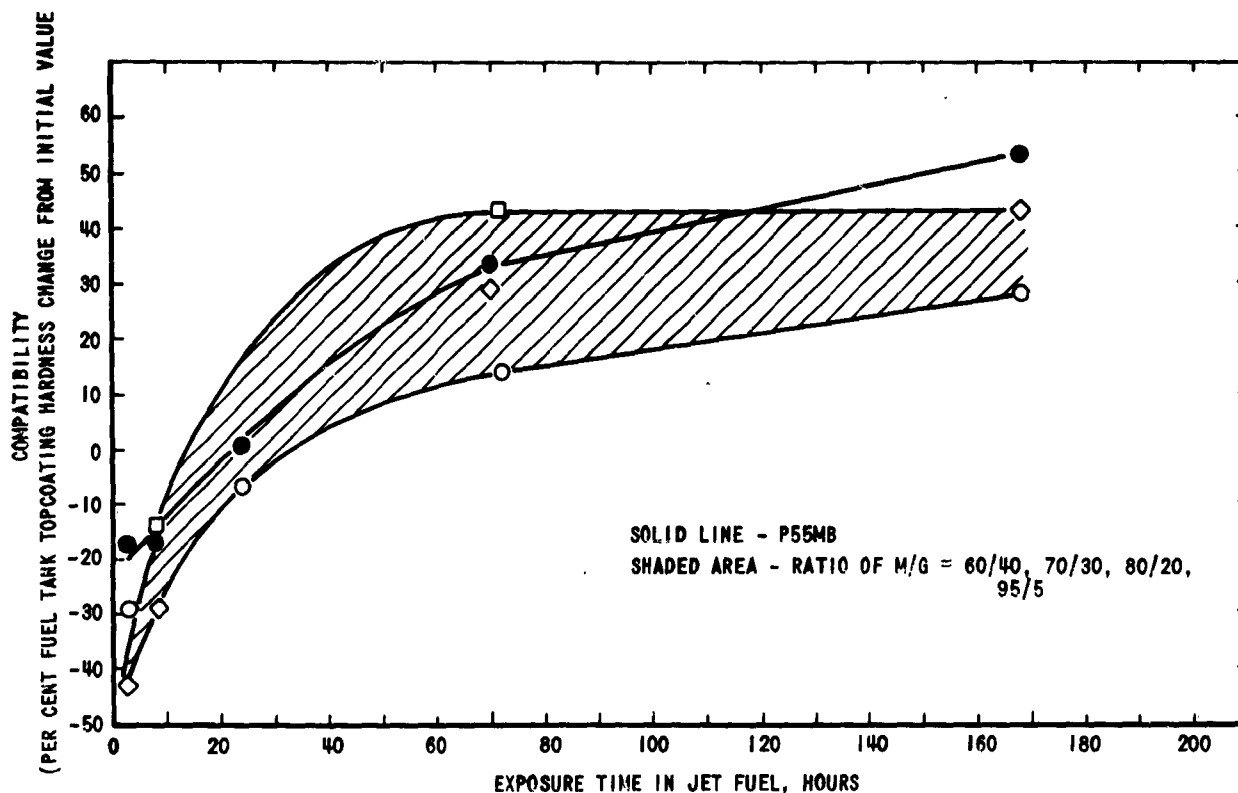
Fig. 33 - Fuel Tank Topcoating Hardness as a Function of Time at
140°F and Ratio of P55MB Additive Components at 0.5
Per Cent Total Additive Concentration in JP-5 Fuel
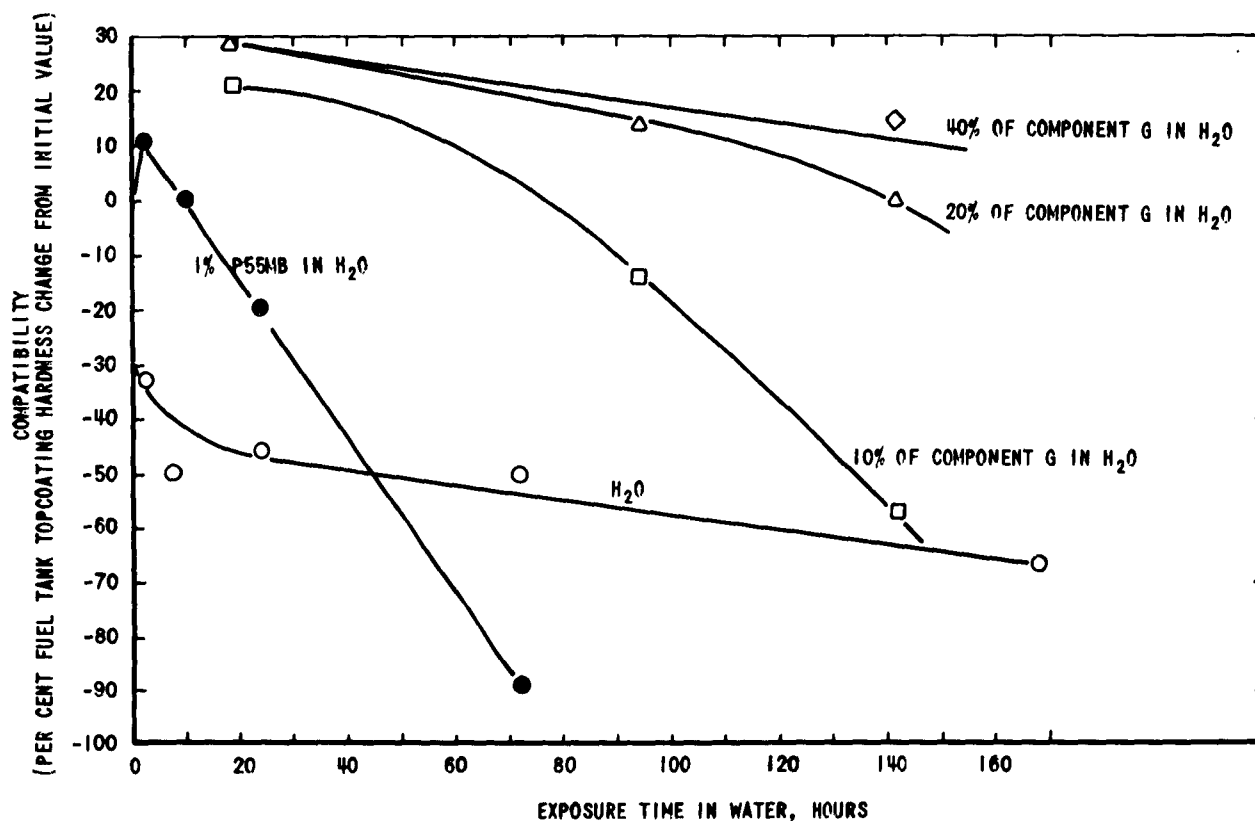
Fig. 34 - Fuel Tank Topcoating Hardness as a Function of Time at
140°F and Concentration of Component G in Water Alone
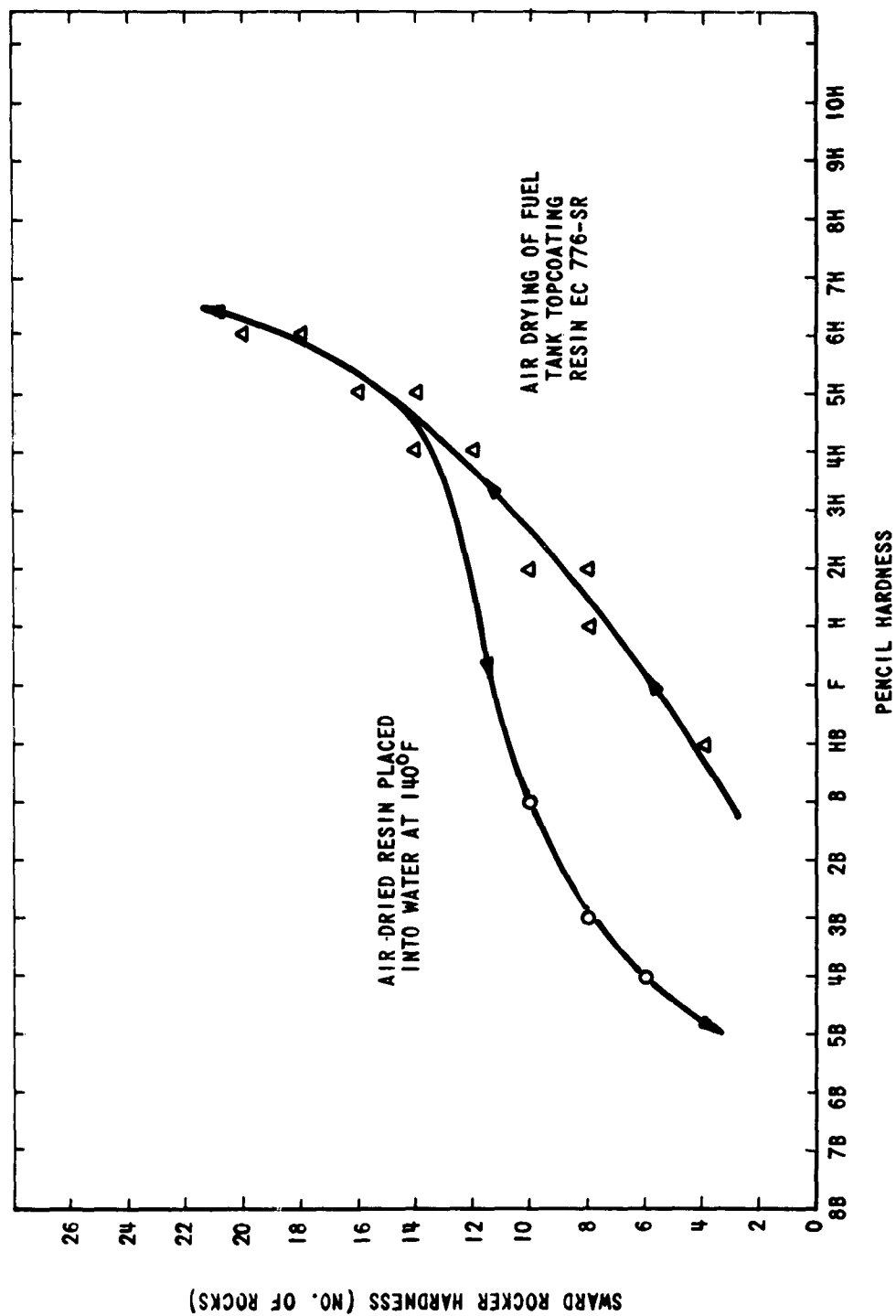
Fig. 35 - Correlation of Sward Rocker Hardness Test with Pencil Hardness Test

TABLE III

THE EFFECTS OF CYCLING THE TEMPERATURE OF THE FUEL-ADDITIVE MIXTURES BETWEEN +140° AND -65°F ON THE FUEL-TANK TOPCOATING

(Results Given as Per Cent Change in Fuel-Tank Topcoating Hardness)

Temperature Not Cycled

Temperature Cycled

P55MB/JP-5

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	+18	+17	+33
168	+32	+42	+53

P55MB/JP-4

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	+5	+5	+5
168	-	-	-

Additive "A"/JP-5

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	+34	+25	+0
168	+34	+27	+8

Additive "A"/JP-4

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	+3	-11	-25
168	-12	-26	-35

P55MB/JP-5

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	0	0	-12
168	0	0	-27

P55MB/JP-4

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	0	+12	-12
168	0	+12	-12

Additive "A"/JP-5

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	+75	-12	-12
168	+75	-12	-12

Additive "A"/JP-4

Time (Hr.)	Concentration (%)		
	0.1	0.3	0.5
72	0	-12	-25
168	0	-12	-25

Scaled-down fuel tanks supplied by Boeing Airplane Company and containing 0.2 per cent P55MB in JP-4 and JP-5 fuels were subjected to temperatures of 140°F and -65°F alternately every week for 14 weeks.

The hardness of the bottom and lid of the fuel tank was measured initially and remeasured at approximately monthly intervals. After each monthly test, fuel was replaced with fresh solution of P55MB in jet fuel. Table IV gives the per cent change in hardness from the initial value of the fuel-tank topcoating on the bottom and the lid of the simulated fuel tanks.

TABLE IV

COMPATIBILITY STUDY ON SIMULATED FUEL TANKS

Sample	Position Measured	% Change in Hardness of Fuel Change Topcoating No. of Months (%)		
		1	2	3
Concentration of P55MB in jet fuel				
0.0% JP-4	Lid	-20	-20	+20
	Bottom	-17	-17	-17
0.2% JP-4	Lid	-50	-5	-17
	Bottom	-25	-25	+25
0.2% JP-5	Lid	0	0	+40
	Bottom	-25	0	-25

Preliminary tests were made to evaluate the use of nonionic surfactants in polar-type anti-icing agents. Surfactants used were Leyco E-160 and Ninox BDO. Anti-icing agents used in combination with the surfactants were: (1) methoxytriglycol, (2) ethoxytriglycol, (3) triethylene tetramine, (4) diethylene triamine, (5) triethanolamine, (6) Additive "A" and (7) tetraethylene glycol.

Table V lists the combinations of surfactants and polar anti-icing additives in which a 1 per cent additive mixture in JP-4 jet fuel remained nearly clear at -65°F.

TABLE V

PROMISING SURFACTANTS AND POLAR ANTI-ICING ADDITIVE
COMBINATIONS AS A JET FUEL ANTI-ICING AGENT

Leyco E-160   and Additive "A"*

Ninox BDO   and Methoxytriglycol

Ninox BDO   and Tetraethylene Glycol

Ninox BDO   and Triethanolamine

Ninox BDO   and Ethoxytriglycol

---

* Additive "A" = Tris [1-(2-methyl) - aziridinyl] -phosphine oxide.

2. Correlation of Pencil Hardness Test With Sward Rocker Hardness Test

Aluminum test panels coated with fuel-tank topcoating resin EC 776-SR were prepared in the same manner as the test panels for the compatibility study (see Section IV, B, 1, p. 37). Both the Sward Rocker Test and Pencil Hardness Test were performed on each test panel.

Nine test panels were prepared, and hardness tests were started as soon as the tackiness disappeared. The test panels were allowed to stand for 48 hr. at room temperature with periodic testing. At that time they were dried at 180°F for 5 min. and retested.

When the panels were near maximum hardness they were placed in water at 140°F for 2 hr., removed, and the hardness measured. Next, the panels were placed in water at 140°F for a total time of 48 hr., and the hardness measured using again both the Sward Rocker and Pencil Hardness Tests.

Figure 35 shows the correlation of the Sward Rocker Test to that of the Pencil Hardness Test for resin EC 776-SR.

The resulting correlation indicates a hysteresis effect. The measured hardness depends upon the cycle in which measurements are being performed (drying or softening of the resin).

V. OVER-ALL RESULTS AND CONCLUSIONS

The results obtained from the storage stability tests indicate that the physical properties of jet fuel do not change in the presence of anti-icing additive P55MB during five months of storage. However, some of the additive is depleted, and will have to be replenished; or a higher concentration of the additive will need to be added at the refinery.

The solution stability of the additive-fuel blend indicates that at lower temperatures the amount of additive extracted into a water phase increases.

The amount of additive extracted into the water phase will not seriously affect the fuel tank topcoating at a concentration of additive in the fuel of 0.1 per cent.

The solubility of the additive in jet fuel decreases with temperature. At -65°F the solubility is $\sim$ 0.3 per cent. Therefore, no loss of additive will occur at a concentration of 0.1 per cent in jet fuel.

The effect of the additive on the growth of microorganisms depends solely upon the type of organisms present.

The anti-icing additive P55MB will be suitable for use in jet aircraft if due precautions are taken.

APPENDIX I

STORAGE STABILITY DATA

TABLE VI

MEASURED VALUES OF JP-4 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Amount of Additive in Drum by Analysis										
0	0.048	0.112	0.218	75	63	0.071	0.138	0.205	62	37
2	0.041	0.108	0.208	49	21	0.067	0.131	0.199	48	28
4	0.045	0.102	0.204	44	33	0.066	0.126	0.197	46	33
5	0.045	0.102	0.197	53	34	0.062	0.124	0.190	50	30
Thermal Stability										
(a) Change in Pressure drop in 5 hr.										
0	2.4	0.35	0.75			1.3	0.70	0.20		
2	0.1	0.05	0.10			0.03	0.04	0.04		
4	0.1	0.05	0.09			0.05	0.03	0.09		
5	0.02	0.01	0.10			0.23	0.15	0.10		
(b) Preheater Deposit										
0	0	0	0			0	0	0		
2	0	0	0			1	0	0		
4	0	0	0			0	0	0		
5	1	0	0			0	1	1		

TABLE VI (Continued)

MEASURED VALUES OF JP-4 JET FUEL PROPERTIES

	No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
		0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Existing Gum (mg/ml)	0	<1.0	1.0	<1.0			<1.0	<1.0	<1.0		
	2	<1.0	<1.0	<1.0			<1.0	<1.0	<1.0		
	4	<1.0	<1.0	<1.0			1.2	2.8	1.8		
	5	<1.0	<1.0	1.2			<1.0	<1.0	<1.0		
Potential Gum (mg/ml)											
(a) Insoluble Gum	0	0.0	0.0	0.0			0.8	0.7	0.7		
	2	0.7	0.0	0.0			0.0	0.0	0.0		
	4	0.8	0.5	1.3			2.8	1.2	0.0		
	5	1.3	0.4	0.4			1.1	0.9	1.0		
(b) Soluble Gum	0	2.1	2.1	1.5			1.6	1.3	1.1		
	2	1.7	1.6	1.4			2.0	1.3	1.2		
	4	1.0	1.8	1.0			1.8	2.2	2.8		
	5	2.0	1.7	1.7			3.9	3.0	3.8		
(c) Precipitate	0	0.0	0.0	0.0			0.0	0.0	0.0		
	2	0.0	0.0	0.0			0.0	0.0	0.0		
	4	0.0	0.0	0.0			0.0	0.0	0.0		
	5	0.0	0.0	0.0			0.0	0.0	0.0		

TABLE VI (Continued)

MEASURED VALUES OF JP-4 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
(d) Total Potential Residue										
0	2.1	2.1	1.5			2.4	2.0	1.8		
2	2.4	1.6	1.4			2.0	1.3	1.2		
4	1.8	2.3	2.3			4.6	3.4	2.8		
5	3.3	2.1	2.1			3.9	3.0	3.8		
Reid Vapor Pressure (psig)										
0	3.4	3.3	3.2			3.4	3.3	3.3		
2	3.5	3.4	3.4			3.4	3.4	3.4		
4	3.5	3.2	3.4			3.4	3.1	3.0		
5	3.4	3.3	3.3			3.0	3.0	3.0		
API Gravity (API)										
0	52.1	52.1	52.1			52.2	52.1	52.1		
2	52.2	52.1	52.1			52.1	52.1	52.1		
4	52.1	52.1	52.1			52.1	52.0	52.0		
5	52.2	52.1	52.1			52.0	52.0	52.0		
Aniline Point (°F)										
0	129.8	129.8	129.6			130.1	130.1	130.1		
2	129.6	129.5	129.4			129.5	129.3	129.3		
4	129.8	129.8	129.7			129.6	129.3	129.4		
5	129.6	129.4	129.5			129.6	129.4	129.4		

TABLE VI (Concluded)

MEASURED VALUES OF JP-4 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Thermal Valve (Aniline-Gravity Product)										
0	6,761	6,763	6,753			6,783	6,770	6,776		
2	6,757	6,741	6,740			6,748	6,738	6,738		
4	6,763	6,768	6,758			6,748	6,724	6,730		
5	6,757	6,740	6,742			6,738	6,730	6,721		
Copper Corrosion Test										
0	1	1	1			1	1	1		
2	1	1	1			1	1	1		
4	1	1	1			1	1	1		
5	1	1	1			1	1	1		

TABLE VII

MEASURED VALUES OF JP-5 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Amount of Additive in Drum by Analysis										
0	0.002	0.094	0.0187	52	40	0.001	0.094	0.195	49	29
2		0.078	0.127	36	28	0.001	0.081	0.167	31	18
4		0.084	0.172	46	26	0.001	0.084	0.168	40	30
5		0.082	0.002*	37	35	0.001	0.079	0.162	58	43
Thermal Stability										
(a) Change in Pressure drop in 5 hr.										
0	1/	2/	3/			1/	222	3/		
2		12.00	20.00			0.5	0.08	0.1		
4		0.10	0.10			0.23	0.1	0.1		
5		0.09	0.11			0.11	0.1	0.9		
		0.09								
(b) Preheater Deposit										
0		0	0			0	0	0		
2		1	1			1	0	0		
4		1	1			0	0	1		
5		0	1			0	1	0		

*   Excess water was found in storage drum.

1/   Change in pressure drop, 25 in. Hg/2 hr.

2/   Change in pressure drop, 25 in. Hg/3 hr.

3/   Change in pressure drop, 25 in. Hg/4 hr.

TABLE VII (Continued)

MEASURED VALUES OF JP-5 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Existing Gum (mg/ml)										
0	<1.0	1.6	<1.0			<1.0	<1.0	<1.0		
2		<1.0	<1.0			<1.0	<1.0	<1.0		
4		<1.0	<1.0			<1.0	<1.0	<1.0		
5		<1.0	<1.0			<1.0	2.6	<1.0		
Potential Gum (mg/ml)										
(a) Insoluble Gum										
0	0.0	0.0	0.0			0.0	0.0	0.0		
2		0.0	0.0			0.0	0.0	0.0		
4		0.0	0.0			0.0	0.0	0.0		
5		0.0	0.0			0.5	0.0	0.0		
(b) Soluble Gum										
0	7.0	12.7	11.0			3.1	6.3	6.7		
2		8.4	6.4			2.7	5.4	7.3		
4		4.9	5.6			1.5	3.1	5.1		
5		4.6	3.7			3.7	4.1	4.6		
(c) Precipitate										
0	0.0	0.0	0.0			0.0	0.0	0.0		
2		0.0	0.0			0.0	0.0	0.0		
4		0.0	0.0			0.0	0.0	0.0		
5		0.0	0.0			0.0	0.0	0.0		

TABLE VII (Continued)

MEASURED VALUES OF JP-5 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
(d) Total Potential Residue										
0	7.0	12.7	11.0			3.1	6.3	6.7		
2		8.4	6.4			2.7	5.4	7.3		
4		4.9	5.6			1.5	3.1	5.1		
5		4.6	3.7			3.7	4.1	4.6		
Reid Vapor Pressure (psig)										
0	0.3	0.2	0.3			0.3	0.3	0.3		
2		0.4	0.3			0.5	0.4	0.4		
4		0.3	0.2			0.5	0.3	0.3		
5		0.4	0.2			0.1	0.2	0.2		
API Gravity (API)										
0	44.8	44.8	44.8			44.8	44.8	44.8		
2		44.6	44.7			44.7	44.6	44.7		
4		44.7	44.7			44.8	44.7	44.6		
5		44.7	44.7			44.7	44.6	44.6		
Aniline Point (°F)										
0	137.0	137.7	136.4			136.4	136.4	136.4		
2		136.1	136.0			135.9	136.2	136.1		
4		136.5	136.3			136.6	136.5	136.6		
5		136.4	136.3			136.3	136.3	136.3		

TABLE VII (Concluded)

MEASURED VALUES OF JP-5 JET FUEL PROPERTIES

No. of Months Stored	Closed Vents Concentration P55MB (%)			Temperature for Day of Sampling		Open Vents Concentration P55MB (%)			Temperature for Day of Sampling	
	0.0	0.1	0.2	Max.	Min.	0.0	0.1	0.2	Max.	Min.
Thermal Value (Aniline-Gravity Product)										
0	6,138	6,125	6,111			6,111	6,111	6,111		
2		6,069	6,073			6,068	6,074	6,075		
4		6,096	6,087			6,111	6,100	6,093		
5		6,098	6,094			6,091	6,082	6,078		
Copper Corrosion Test (Class)										
0	1					1	1	1		
2		1	1				1	1		
4		1	1				1	1		
5		1	1				1	1		

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MIDWEST RESEARCH INSTITUTE, Kansas City,Mo.
EFFECTS OF ANTI-ICING ADDITIVES ON JET FUEL
PROPERTIES, by D. A. Netzel, T. J. Byerley,
and H. B. Pollock. May 1961. 60p. incl.
figs., tables. (Project 3048; Task 30178)
(ASD TR 61-280)
(Contract No. AF 33(616)-7598)
                    Unclassified Report

The storage stability over a five-month
period of jet fuels containing anti-icing
additive P55MB has been investigated. The
tests included (1) thermal stability, (2)
gum content, (3) API gravity, (4) aniline
point, and (5) sulfide content. Fuel con-
tamination and microorganism growth due to

1.   Fuel Additives -
         Application
2.   Fuel Additives -
         Determination
3.   Fuel Additives -
         Effectiveness
4.   Fuel Additives -
         Physical
         Effects
5.   Fuel Additives -
         Test Results
I.   Netzel, D. A.
II.   Byerley, T. J.

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the additive were also studied. The solu-
tion stability (partition coefficient,
solubility, and "coupling effect") of
P55MB anti-icing additive-fuel blends have
been determined. Also, determined were the
effects of anti-icing additives P55MB and
Additive "A" on the hardness of the topcoat-
ing of the fuel tanks. A graphical relation-
ship is given between the Sward Hardness
Test and the Pencil Hardness Test used to
measure the hardness of the fuel-tank top-
coating.

UNCLASSIFIED

III. Pollock, H. B.
IV.   Aeronautical Sys-
         tems Division
V.   Contract No. AF
         33(616)-7598

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